

PRINCIPLES AND APPLICATIONS
OF
Electrochemistry

IN TWO VOLUMES

Volume II — APPLICATIONS

By

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PREFACE TO THE SECOND EDITION

This volume covers the applications of electrochemistry; the principles of electrochemistry are discussed by Dr. H. Jermain Creighton in Volume I. It is our hope that the two volumes will adequately cover, where a great deal of detail is not required, the whole field of electrochemistry. For those who desire to pursue the subject still further, a large number of references have been given.

In preparing this volume on the applications of electrochemistry I have had in mind two classes of readers: students in universities, colleges, and technical schools, who will use it as a textbook; and persons connected with the industry who might want to use it as a reference work.

I have found myself confronted with the difficult problem of making the book sufficiently complete and up-to-date without at the same time making it too voluminous for the use of colleges or technical schools, where the time allotted to the study of electrochemistry is necessarily limited. I hope I have struck a balance satisfactory to most of the readers.

In this revised edition I have followed in the main the same general arrangement and grouping of topics as in the first edition. Considerable new material has been added, and some of the former material has been condensed and some omitted entirely.

In giving statistics on production I have had considerable difficulty in deciding what year to use for the purpose, for we have not had a "normal" production year for well over a decade. I have therefore in a few cases used the production figures for 1929; in most cases figures for that year would now be meaningless and current figures have been used.

References to the literature have been given freely. The purpose of the references is to offer ready means for further study and to give proper credit for the material presented. It is obvious, however, that to attempt to give full credit would be tedious to the reader and would be impossible of attainment. This book is based on notes and literature accumulated over a period of eighteen years of teaching the applications of electrochemistry; during that time much information has been obtained by correspondence, conferences, and personal contacts, but the exact source of some of the information cannot now be traced.

Throughout the text acknowledgments have been made to individuals who have supplied special information. Many firms have supplied

illustrative material, and credit has been given in connection with the respective illustrations. To all who have helped in various ways I express my sincere thanks. It would be presuming for an individual to try to cover without help as large a practical field as is presented in this text. I again feel fortunate in having obtained help, advice, and criticism from a number of persons connected with various industries. I express my thanks to the following: William Adam, Jr., Vice President, Ajax Electric Company; W. H. Aldrich, Superintendent, Leaching Plant, Inspiration Consolidated Copper Company; E. W. Allen, Manager of Engineering, and K. W. Bailey, Thomas A. Edison, Inc.; K. Harms, American Smelting and Refining Company; Samuel Arnold, 3rd, Pittsburgh, Pa.; K. Schumpelt, Baker and Company, Inc.; W. Blum, National Bureau of Standards; Oliver Bowles, U. S. Bureau of Mines; F. H. Chapman, Consolidated Mining and Smelting Company of Canada, Ltd.; A. S. Albright, Acting Chief of Research, The Detroit Edison Company; George Easter, Assistant Director Research Laboratory, The Carborundum Company; R. N. Sackett, Eastman Kodak Company; C. W. Eichrodt, Phelps Dodge Refining Corporation; W. L. Hammerquist, Research Engineer, Electro Manganese Corporation; J. H. Critchett, Vice President, Electro Metallurgical Company; H. S. Walker, Baker and Adamson Division, General Chemical Company; W. J. Walker, Electronic Tube Engineer, and L. R. Koller, Research Laboratory, General Electric Company; George W. Heise, National Carbon Company; John L. Hutton, General Manager, T. Shriver and Company; R. L. Peek, International Nickel Company; W. B. Wallis, President, Pittsburgh Electro-melt Furnace Corporation; R. R. Ridgway, Associate Director of Research, Norton Company; E. W. Rouse, Jr., The Wilsco Corporation; H. W. Abbot, Director of Laboratories, Speer Carbon Company; Dr. L. D. Vorce, Westvaco Chlorine Products Corp.; P. H. Brace, Consulting Metallurgist; and W. G. Woolf, Superintendent Electrolytic Zinc Plant, Sullivan Mining Company.

In addition, a number of readers of the first edition have sent in helpful suggestions for revisions, or have called attention to inaccuracies. To these I express my thanks and hope that they and others will do the same for this edition.

Several manufacturers and periodicals have supplied new illustrations; acknowledgment is made in connection with each illustration.

W. A. KOEHLER

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CHAPTER I

ECONOMICS OF POWER GENERATION

Practically all electrochemical and related processes require unidirectional current, the outstanding exception being for electric furnaces, in which alternating current is used. In most instances the voltage required is relatively low and the amperage high. A notable exception is found in the electrostatic precipitation of dust and fume, where direct-current voltages up to 100,000 volts may be required, and the current consumed is almost negligible.

A few exceptional small electrochemical plants may be able to purchase direct current at approximately the desired voltage, but ordinarily the direct current must be supplied at the plant.

Direct-Current Power Supply. The direct current required in an electrochemical industry may be obtained in several ways. The most desirable method will depend upon the nature of the process, the amount of energy required, and the local conditions, but even when all these factors are carefully considered it may not be possible to decide definitely on a particular method or a particular type of equipment.

Many plants find it advantageous to purchase their power, which is delivered at the plant as a high-voltage alternating current. The line voltage is stepped down in transformers to a convenient voltage so that it can be converted to direct current. This conversion may be made by (a) synchronous converters, (b) motor-generators, and (c) rectifiers.

Synchronous converters find wide application in electrochemical industries for converting alternating to direct current. The advantages of a synchronous converter over motor-generators are: lower first cost (if the cost of special transformers is not included), smaller floor space required, and higher efficiencies. The synchronous converter underwent its greatest development during the two decades from 1910 to 1930, after which construction of new units declined very much. This was due chiefly to the introduction of newer and less costly conversion devices, such as the steel tank mercury-arc rectifier and the ignitron. The efficiency of a converter is generally above 92 per cent and may be as much as 94 per cent. An installation of synchronous converters is shown in Fig. 1.

Motor-generators are also widely used for converting alternating current to direct current. The advantages of the motor-generator over the synchronous converter are: wider voltage adjustment, overcompounding, and power-factor correction when driven by a synchronous motor. Also, when motor-generators are driven by synchronous motors the direct-current voltage does not fluctuate with changes in the power-line voltage. Motor-generators are used for converting alternating to direct current



FIG. 1. Eighteen synchronous converters used in aluminum production. (*Courtesy General Electric Company.*)

and also for converting alternating current of one frequency to that of another frequency, as is necessary in the operation of low-frequency, open-channel type of induction furnaces. Motor-generators of the smaller type are widely used for charging storage batteries and for electroplating. Motor-generators for electroplating are discussed in Chapter V. A motor-generator set used for electroplating is shown in Fig. 40, page 96.

Rectifiers of various types are available for converting alternating current to unidirectional current. Their operation is described elsewhere in this volume. The *electrolytic rectifier* (p. 545) is used where but small amounts of current are needed. It is suited for trickle charging of storage cells and can be used for experimental electroplating if direct current from other sources is not available.

The *thermionic rectifier* (p. 473) is widely used for charging storage cells. This rectifier is called a *Tungar* rectifier by the General Electric Company and a *Rectigon* by the Westinghouse Electric and Manufacturing Company. These are built in several sizes, a common size being one that supplies 3 to 6 amp. of direct current at 5 to 6 volts, respectively, from 110-volt, 60-cycle service mains. Another type of thermionic rectifier is the *Kenotron*. It differs from the Tungar type in that the bulb is highly exhausted. A Kenotron is especially adapted for converting alternating current at high voltage and is well suited for use in connection with electrostatic precipitators. A certain size Kenotron is rated at 100,000 volts on the direct-current side and is capable of rectifying 100 ma. when used as a half-wave rectifier. A Kenotron does not become comparable in efficiency to a high-power transformer (98 per cent) until the voltage reaches the order of 100 kv.

The *mercury-arc* rectifier finds its greatest usefulness in a field lying between those of the Tungar and the Kenotron. Mercury-arc rectifiers can be constructed having capacities of hundreds of kilowatts. For small capacities within the Tungar or Rectigon range, the cost of the automatic starting equipment for the mercury-arc rectifier usually directs the choice to one of the former. For low voltages of 100 volts or less, combined with larger currents (over 15 amp.), the losses in a mercury-arc rectifier are high enough so that motor-generators may have higher efficiencies at full load, but at light or intermittent loads the small standby losses of the mercury-arc rectifier may give it an advantage over the motor-generator. The steel tank mercury-arc rectifier (p. 477) has come into considerable industrial use since 1929 when it began to replace the synchronous converter for electric railway service, and when the first units for electrochemical work in North America were installed at Trail, B. C., to supply 650 volts for hydrogen and oxygen cells; they are now operating successfully under practically every type of electrochemical load. Mercury-arc-rectifier losses are practically the same at any voltage, and above 600 volts it is difficult to find any device giving greater efficiency and economy.¹ The ignitron (p. 479) has come into use rapidly since its commercial introduction in 1937. It is a type of mercury-arc rectifier in which each anode and cathode is enclosed in an individual evacuated chamber. It is being applied in the aluminum industry for supplying direct current for the reduction cells, and in a variety of other electrochemical industries.

In some cases it may be more desirable to generate the electrical energy at the plant. This may involve first the generation of alternating

¹ D. C. Prince and F. B. Vogdes, *Principles of Mercury Arc Rectifiers and Their Circuits*, McGraw-Hill Book Company, New York, 1927.

current and then its conversion to direct current by one of the means discussed above. On the other hand, direct current may be generated directly at the desired voltage. Either alternating or direct current may be generated by using as a prime mover: (a) steam turbines, (b) steam engines, (c) internal-combustion engines, and (d) water wheels or turbines. Figure 2 shows an installation of steam-turbine-generator sets.

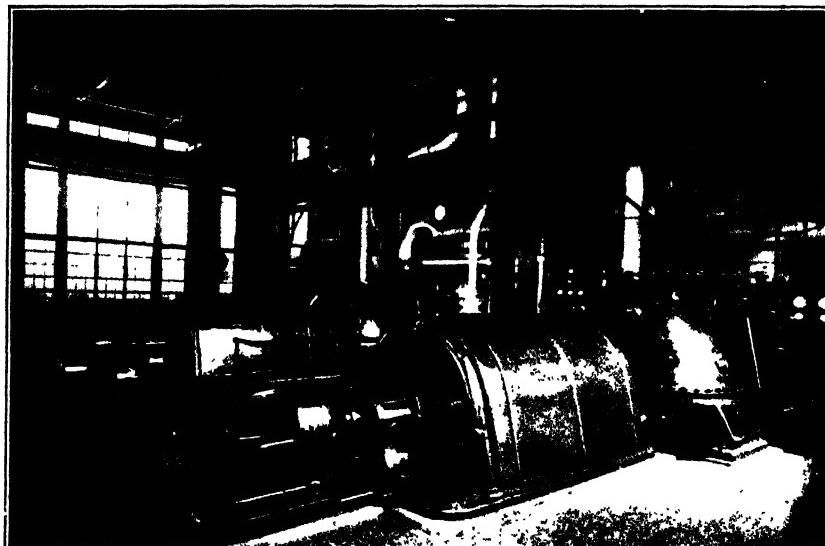


FIG. 2. Two condensing double-automatic extraction steam-turbine-generator sets used for cyanamide production. Each generator delivers 3,000 kw., 60 cycles.
(Courtesy General Electric Company.)

Power Costs. Costs of purchased power are divided into two parts, the demand charge and the energy charge. The demand charge is based entirely upon the total kilowatts or horsepower demanded by the consumer at any one time during the billing period. This period is usually for one month, but some companies permit the customer to use the year as the unit. It is also common practice not to count any "peak" in the load that has a duration of less than a certain stated time, generally a period of 15 minutes but sometimes 30 minutes or even an hour. The demand charge also is rated in "blocks," the charge being less per kilowatt or per horsepower for succeeding blocks. For instance, in one locality the demand charge is \$5 per kw. for the first 25 kw. of demand, \$2 per kw. for the next 75 kw. of demand, and \$1 per kw. for all demand in excess of the first two blocks.

The energy charge is based on the actual kilowatt-hours consumed. This charge is also divided into blocks. Thus, in the locality for which

the demand charges are given above, the energy charge is 1 cent per kw-hr. for the first 30,000 kw-hr., and 0.75 cent per kw-hr. for all in excess of that amount.

There is generally a minimum charge also, which usually covers a period of 1 month but occasionally a period of 1 year. In many cases the minimum charge is equal to the demand charge, but other bases are also in common use.

A discount is ordinarily allowed for prompt payment, or a penalty is charged for deferred payments. Quantity discounts may also be allowed. In one locality in Washington this discount amounts to nothing on the first \$200, 20 per cent on the next \$100, and 30 per cent on the next \$100. A discount may be allowed for power used at off-peak periods. This may apply to the demand charge or to the energy charge, or different rates may apply to peak and off-peak loads. The variations between peak and off-peak demand charges are illustrated by the following table, which applies to a large mid-western city:

DEMAND CHARGES PER KILOWATT

	Peak	Off-Peak
First 100 kw.	\$2.15	\$1.50
Next 100 kw.	1.85	1.35
Excess	1.60	1.10

The peak hours depend upon local conditions. In the above city they begin between 4:30 and 6 P.M., depending upon the time of year, and end at 7 P.M.

The nature of the power factor of the load may also carry a discount or a penalty. In a city in Pennsylvania, for example, the demand for billing purposes is decreased by $\frac{1}{2}$ per cent for each 1 per cent the average power factor is above 85 per cent lagging (provided that the maximum limit is 100 per cent power factor), and similarly increased if the power factor is below 85 per cent lagging.

Frequently, if the energy is generated by steam, the contract carries a clause to provide for a change in the energy rate should the price of coal vary a certain amount. Thus, one company in New York City in 1932 increased or decreased the energy charge 0.008 cent per kw-hr. for each 10 cents of increase or decrease below \$5.50 per long ton in cost of bituminous coal, alongside the company's docks.

Other factors may affect the power costs, such as whether the power is alternating or direct current, the frequency or number of phases demanded, and the voltage the customer can use.

Practically always the rates are based on the class of service demanded. The classes of service offered by one company in a southern city are

ECONOMICS OF POWER GENERATION

TABLE I
ELECTRICAL POWER COSTS AT VARIOUS LOCALITIES

City or Country	Source of Power	Class of Service	Minimum Charge per Month	Monthly Charge per Kw. of Demand	Energy Charge per Kw-Hr.
Berkeley, Cal.	Steam and hydroelectric	Electrochemical and metallurgical	\$ 875.00	\$4.375-3.50	\$1.00-0.75
Birmingham, Ala.	Steam	Large lighting and power	125.00	5.00-1.00	1.25-0.60
Brooklyn, N. Y.	Steam	Large power	225.00	2.25-1.25	2.00-0.80
Charleston, W. Va.	Steam	Primary power	75.00	1.50	
Chicago, Ill.	Steam	Large lighting and power, outer zone	50.00	2.00	2.70-0.40
Cleveland, O.	Steam	Industrial lighting and power	0.75/kw.	2.00-1.00	1.50-0.50
Milwaukee, Wis.	Steam and hydroelectric	Large power and lighting	1,560/yr.	31.20-16.80	1.90-0.95
Montreal, Canada	Hydroelectric	Primary power	1.00/hp.	1.00/hp.	1.50-0.50
Niagara Falls, N. Y.	Hydroelectric	Primary lighting and power	60.00	1.00-0.75	1.00-0.60
Ottawa, Canada	Hydroelectric	General power	0.80/hp.	0.80/hp.	1.30-0.12
Pittsburgh, Pa.	Steam	Large lighting and power	20 kw.	1.50-1.00	6.00-0.70
Pittsburgh, Pa.	Steam	Battery charging	7.50+	...	3.25 a.c.
Seattle, Wash.	Hydroelectric	General power	1.00/hp.	4.00-1.00	4.225 d.c.
England	0.50-0.40
Germany	0.40-0.36
Norway	...	Hydroelectric	1.50-1.00
Sweden	...	Hydroelectric	1.50-1.00
Switzerland	...	Hydroelectric	0.30

typical of many others: residence service, general lighting, battery charging, large lighting and power (the customer guaranteeing a monthly demand of at least 25 kw.), display lighting, general power, large power (the customer guaranteeing a monthly demand of at least 50 kw.), large power, optional (the customer guaranteeing a monthly demand of at least 100 kw.). Taking the country as a whole, many dozens of classes of service are available, each carrying its own demand charge, energy charge, minimum charge, and special discounts. A special class of service for electrochemical processes is a rare exception. The classes of service offered throughout the country and the demand and energy charges lack systemization. Nearly every company has a system and rate peculiarly its own, having been developed, presumably, to fit local conditions.

Some information regarding power costs in various cities in the United States and Canada and isolated instances in European countries is given in Table I. The table, however, is insufficiently complete for a criterion as to the actual cost at any locality. Under demand charges and power charges, the first figure represents the charge for the first block, the last figure that for the last block. The size of the blocks and the number of blocks vary greatly so that no true comparisons can be made without knowledge of the number of blocks and the rate charged in each one. The table is given more as a general indication of the range of prices charged. More complete information is provided in government publications.² The Federal Power Commission has also made a study of the power requirements in some of the leading electrochemical industries.³

² "Typical Electric Bills," Federal Power Commission, Washington, D. C., 1940.

³ "Power Requirements in Electrochemical, Electrometallurgical and Allied Industries," Federal Power Commission, 1938.

CHAPTER II

REVIEW OF THEORETICAL ELECTROCHEMISTRY

It is not the purpose in this volume to present any lengthy discussion of the principles of electrochemistry. They are comprehensively discussed by Creighton in Volume I, and the student is urged to familiarize himself with the contents of that volume. Yet, for the sake of the convenience of the reader and as a basis for our discussion of the applications of electrochemistry, it is considered advisable to assemble definitions of some of the more commonly used terms in electrochemistry and to give a brief review of some of the principles involved. The student, however, should bear in mind that a more thorough study of the principles as presented in Volume I will be a great aid in a fuller understanding of the subject.

Polar and Non-Polar Molecules. In order to comprehend some of the phenomena encountered in electrochemistry it will be helpful to have some knowledge of the fundamentals of atomic structure. When Dalton published his first work on atomic theory in 1808, he postulated the existence of minute particles called atoms; these he considered invisible. According to this theory, each species of atom consisted of material characteristically its own, and different from the material that constituted other atoms. Accordingly, there would be as many basically different materials as there are elements, namely 92. Rutherford¹ gave us the modern concept of the nuclear atom; according to this, there are only two basically different kinds of material: both are charges of electricity, one positive, called the proton; the other negative, called the electron. All atoms are made up of these two kinds of charges, and every atom has an equal number of positive and negative charges, but different elements have a different total number of charges, and the charges are arranged differently.

Bohr,² Lewis,³ and Langmuir⁴ have contributed most prominently to our present concept of the arrangement of the protons and electrons

¹ C. T. R. Wilson, *Proc. Cambridge Phil. Soc.*, **9**, 333 (1897); *Phil. Mag.*, **1**, 681 (1904).

² N. Bohr, *Nature*, **112**, July 7 (1923).

³ G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

⁴ I. Langmuir, *ibid.*, **41**, 868, 1543 (1919); **42**, 274 (1920).

in the various atoms. They have developed the hypothesis of a system of atomic structure consisting of a center, called a nucleus, and grouped around this, electrons, resembling in a rough way our solar system. The hydrogen atom is the simplest; it consists of a proton as the nucleus and an electron some distance from it. In all atoms, nearly all the mass is centered in the protons, and all protons are in the nucleus; the mass of a proton is 1,845 times the mass of an electron. The distance between the electron and the proton in an atom of hydrogen is very many times the diameter of the proton, so the atom is nearly 100 per cent empty space. According to Bohr's theory, all electrons are in rapid motion about the nucleus. Physicists generally accept this theory, and on that basis have made some interesting calculations and predictions that have harmonized with known facts. The nucleus of a hydrogen atom consists of a single proton; all other nuclei contain protons, charged positively, and also neutral particles called neutrons. A neutron has practically the same mass as a proton, but it has no electrical charge. The charges on the electrons and protons are equal in magnitude but opposite in sign. The total number of electrons and protons in any atom are equal, and all atoms are therefore electrically neutral.

An atom, then, consists of a nucleus containing protons and neutrons and surrounding the nucleus one or more imaginary shells containing electrons. The electrons are believed to move around the nucleus not in perfectly regular orbits but in paths that are continually changing. The terms "shells" and "orbits" are commonly used interchangeably.

As a result of Moseley's work each atom can be assigned a number and the atoms can be arranged in the order of these atomic numbers. The atomic number of an atom is equal to the number of protons in the nucleus, which is also equal to the number of electrons surrounding the nucleus. The sum of the protons and neutrons in a nucleus correspond to the atomic weight of the atom.

The electrons in the outer shell of an atom are called valence electrons and are the ones that interest us most in electrochemistry.⁵

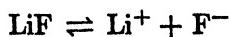
It is assumed that in a chemical reaction electrons are given up from the valence shell by one or more atoms and at the same time these electrons are acquired by the valence shells of another atom or atoms, or, instead, electrons may be shared by two or more electrons.

The hydrogen atom is the lightest and simplest in construction of all atoms. The nucleus consists of one proton, with one electron in the orbit. The helium atom contains two protons and two neutrons in the nucleus and two electrons outside the nucleus. Lithium contains three

⁵ In writing equations, \ominus is used to represent an electron. Some writers use e , others ϵ , for this purpose.

protons in the nucleus and three electrons outside the nucleus. Two of these electrons form one shell, just as they did in the helium atom; the other electron is in a new outer shell. Lithium is the first element of its period in the periodic table. Beryllium, the next element to the right, contains one more proton in the nucleus and one more electron in the outer shell. The other elements in the period change progressively, each one to the right having one more proton in the nucleus and one more electron in the outer shell than the preceding one until neon is reached in group 0. It has ten protons in the nucleus, two electrons in the inner shell, and eight electrons in the outer shell. The next period develops in a similar way; a new outer shell is formed, sodium has one electron in this new shell, magnesium two, and so on toward the right to argon which like neon has eight electrons in the outer shell, a total of eighteen electrons and eighteen protons. The neutrons also vary as a rule from atom to atom, but not so uniformly, and two different elements may have an equal number of neutrons in the nucleus.

In this way it is possible to construct a picture of all the atoms, although the structure becomes more complicated for elements having higher atomic numbers. The elements with the valence shells completely filled (or completely empty) are the most stable. Atoms therefore have a tendency to make their outermost shells stable by acquiring more electrons or giving up electrons; this can be accomplished through chemical combination. Those atoms having less than four electrons in the outer shell attempt to part with them by sharing them with, or giving them to, one or more other atoms through chemical combination. Those atoms having more than four electrons in the outer shell attempt to complete the octet by adding one to three electrons which they take from or share with other atoms through chemical combination. Thus, lithium will combine with fluorine, the one electron of the outer shell of the lithium atom fitting into the one vacant space of the incomplete octet of the fluorine atom. Here the electron is transferred bodily from the lithium atom to the fluorine atom; the fluorine half of the LiF molecule has gained an electron and therefore is negative; the lithium end has lost an electron and is positive. In other words, such a molecule has polarity and is called a polar compound. The ions of a polar compound are held together by electrostatic attraction, but when the molecule is dissolved in water, the ions can separate, and if electrolyzed, the two parts are attracted to poles of opposite charges. This separation, due to solution, is represented by the equation



and is spoken of as the process of ionization or preferably dissociation.⁶ Polar compounds form the large group of acids, bases, and salts generally called electrolytes.

Instead of the electron leaving one atom and completely transferring itself to another atom as in lithium fluoride and other polar compounds, there can be chemical combination by a sharing of the valence electrons. Such molecules are not polarized, for one atom has not actually given up any electrons and another has not gained any; both share the same electron or electrons. Such molecules, therefore, are not polarized, they contain no ions, and when dissolved in water they will not conduct an electric current. Organic compounds are of this class of compounds, called non-polar compounds. The above picture of polar and non-polar molecules is presented in this form on account of its simplicity and may not be a true presentation of the nature of the molecules. In Volume I, Creighton gives a more complete discussion of the subject on the basis of a symmetrical (non-polar) and unsymmetrical (polar) arrangement of the atoms of the molecule.

Only enough of atomic structure is presented here to give a concept of its nature and of the sources of ions and their charges in polar compounds. As the atomic number of the atoms increases, the structure becomes more complex. The student is referred to almost any modern textbook in physical chemistry for further discussion of this subject.

Electrolytic Dissociation Theories. In 1887 Arrhenius⁷ formulated his theory of electrolytic dissociation. This theory has enjoyed practically universal adoption and has been a factor of great importance in the development of chemistry. It is presented by Creighton in Volume I, and its fundamentals are so well known that its detailed presentation will not be undertaken here. However, it must be borne in mind that a useful theory by virtue of its apparent plausibility may actually hinder progress by arresting development of more practical theories. Newer scientific developments have helped to expand the theory of Arrhenius and to modify some general concepts. For instance, X-ray studies indicate that sodium chloride crystals are not built up of NaCl molecules but of Na⁺ and Cl⁻ ions arranged in a space lattice with no Na⁺ ion belonging to any specific Cl⁻ ion to form a molecule. When

⁶ According to our present knowledge, the ions exist in the molecule or crystal of a polar compound. When such a compound is dissolved in water, dissociation takes place. Water is the most common solvent causing dissociation, but ammonia, sulphur dioxide, hydrocyanic acid, and hydrofluoric acid all in their liquid state act in a similar way. Organic acids and alcohols also cause some dissociation, though to a lesser degree, but liquid hydrocarbons cause practically no dissociation when polar compounds are dissolved in them.

⁷ S. Arrhenius, *Z. physik. Chem.*, 1, 631 (1887).

such a crystal is dissolved in water the ions lose their systematic arrangement and tumble apart. This concept has not as yet changed our general method of writing equations indicating dissociation:



Most, if not all, ions in aqueous solution are hydrated, that is, they are combined with water, so that, although we commonly represent the copper ion as Cu^{++} , some of the ions are hydrated and have the formula $\text{Cu}(\text{H}_2\text{O})_4^{++}$. Likewise there exist Co^{++} and at the same time $\text{CO}(\text{H}_2\text{O})_6^{++}$ ions, and Cr^{+++} and $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ ions. Similar conditions hold for most ions. In ordinary writing of reactions involving ions, the water of hydration is omitted.

The ionization theory of Arrhenius was attacked by Kahlenberg,⁸ in 1902, who pointed out some of its shortcomings. These attacks did not receive much support by chemists in general, but, as new scientific developments have brought new facts to light, the theory has been strongly attacked, and newer theories have been proposed. Notable among these is that of Debye and Hückel⁹ discussed in Volume I. Arrhenius's theory assumes partial dissociation of electrolytes at strong concentrations increasing to complete dissociation at what is called infinite dilution, thus accounting for the deviation of the osmotic properties of electrolytes from the gas law, $PV = nRT$.

The newer theories assume substantially complete dissociation at all concentrations. Investigations indicate that the electric charges on the ions set up electrostatic fields which limit the free movement of the ions as demanded by the gas laws. Ions of a given sign will be surrounded mainly by ions of opposite sign, and the free movement of all these ions is restricted. On dilution, the ions separate more and more and the effect of the electrostatic attraction of the ions is less marked, at infinite dilution becoming insignificant, so that the gas laws hold.

Degree of Dissociation. Returning to the classical dissociation theory of Arrhenius, when polar compounds are dissolved in water, generally not all the molecules dissociate into ions unless the dilution is very great. The proportion of the total number that dissociate in any particular compound depends upon the nature of the compound, the temperature, and the concentration. If the solvent is other than water, that too will affect the degree of dissociation. The degree of dissociation is expressed as the percentage dissociation divided by 100, and is represented by α .

⁸ L. Kahlenberg, *J. Phys. Chem.*, **8**, 1 (1902).

⁹ P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923); **25**, 97 (1924); see also P. Debye, *Trans. Am. Electrochem. Soc.*, **51**, 499 (1927).

When $\alpha = 0$ none of the molecules have dissociated; when $\alpha = 1$ all have dissociated. The value for 100α gives the percentage dissociation. Table II shows the percentage dissociation (100α) of some of the more common electrolytes.¹⁰ This shows also how the dissociation varies with concentration.

TABLE II

DISSOCIATION OF VARIOUS COMPOUNDS AT 18° C. EXPRESSED AS 100α

Compound	Concentration in Gram-Equivalents per Liter			
	0.001	0.01	0.1	1.0
NaCl	97.7	93.6	85.2	74.1
KCl	97.9	94.1	86.0	74.2
NaNO ₃	97.7	93.2	83.2	66.0
AgNO ₃	97.7	93.1	81.4
Uniunivalent	98.	93.	83.
MgSO ₄	87.3	66.9	44.9	34.9
ZnSO ₄	85.4	63.3	40.5	30.9
CuSO ₄	86.2	62.9	36.9	30.9
Bibivalent	86.	65.	41.
MgCl ₂	95.5	88.3	76.5	66.9
K ₂ SO ₄	95.4	87.2	72.2	59.2
CaCl ₂	95.4	88.2	76.4	66.2
Unibivalent	85.	87.	75.
HCl	99.0	97.2	92.0	79.1
HNO ₃	99.0	96.9	92.0	82.3
NaOH (25° C.)	97.1	93.3	90.5	73.6
CH ₃ CO ₂ H	11.7	4.17	1.34	0.38
NH ₄ OH	11.7	4.07	1.31	0.37

Increase in temperature suppresses the degree of dissociation and therefore tends to reduce the conductivity of an electrolytic solution, but up to a certain temperature the conductivity actually increases with rise in temperature. This appears to be caused by an increase in the velocity of the ions due to decrease in viscosity of the water, which more than compensates for the depressed dissociation. In most electrolytic solutions studied,¹¹ a temperature is reached beyond which the depressed dissociation more than offsets the decreased viscosity and the conductiv-

¹⁰ Compiled from data by Creighton, Vol. I; A. A. Noyes and K. G. Falk, *J. Am. Chem. Soc.*, **34**, 474 (1912).

¹¹ A. A. Noyes and W. D. Coolidge, *Carnegie Inst. Wash. Repts.*, **63**, 340 (1907).

ity decreases. For hydrochloric, nitric, and sulphuric acid solutions, the point at which the temperature coefficient of conductivity changes from positive to negative is between 100° and 240° C. (212° and 464° F.).

FUNDAMENTAL UNITS AND DEFINITIONS

It is fortunate for those who have occasion to use electrical units in electrical and electrochemical engineering that practically no confusion exists in the fundamental units employed. There is in practical use but one unit of current strength, the ampere; one pressure unit, the volt; one resistance unit, the ohm. There are, to be sure, units of other magnitudes, the electrostatic unit of current equal to 3×10^8 amp., the abampere, equal to 10 amp., likewise the abvolt, and so on, but these do not concern us in industrial electrochemistry. Likewise the main units are divided into units of different magnitude so that we have the milliampere and millivolt, but their prefixes clearly indicate their magnitudes.

Electrical Units. Electric current refers to the rate of transfer of electricity. The practical unit of current is the *ampere*; it is defined as that unvarying electric current which, when passed through a solution of silver nitrate, AgNO_3 , under certain specified conditions, will deposit 0.00111800 g. (1.11800 mg.) silver per second. The precise determination of this unit requires considerable experimental ability and especially suitable apparatus. This will be discussed briefly later under coulometers. One ampere will also deposit 0.0003294 g. (0.3294 mg.) of bivalent copper in 1 second. The name "ampere" was chosen in honor of A. M. Ampère (1775–1836), a French physicist and chemist.

An electric current flowing through any medium meets with resistance, the amount depending upon the nature of the conductor, its shape, and its temperature. The unit of electrical resistance is called the *ohm*, named after the German physicist, G. S. Ohm (1787–1854). One international ohm is equal to the resistance offered by a column of mercury 106.3 cm. long and 1 sq. mm. in cross-section at 0° C. (32° F.). Such a column of mercury has a mass of 14.4521 g., so that an ohm may also be defined as the resistance of a mercury column 106.3 cm. long, of uniform cross-section, and weighing 14.4521 g.

In order that the resistances of various materials may be compared it is necessary to establish the shape of the resistor and also the temperature. A commonly accepted shape is that of a cube, the current flowing from one face to the opposite one. The resistance of such a cube is called the *specific resistance* or the *resistivity*. In stating the resistivity of a material the unit should always be mentioned; the term "ohm-

"centimeter" is commonly used, denoting the resistance, expressed in ohms, of a centimeter cube of the material under consideration.

The resistance of a conductor of uniform cross-section is inversely proportional to the cross-sectional area and directly proportional to the length. If total resistance of the conductor under consideration, of uniform cross-section, is known, the specific resistance can be calculated from the equation:

$$r = \frac{Ra}{e}$$

r = specific resistance
 R = total resistance
 a = cross-sectional area
 e = length

The resistance of all metals increases with increasing temperature; the resistance of carbon and graphite and some other substances decreases with increase in temperature. The resistance of many electrolytic solutions used industrially decreases with increasing temperature up to a certain point, owing to the greater mobility of the ions, beyond which the resistance increases, because of the depressing effect of increasing temperature on the degree of dissociation. The change of resistance of conductors with temperature is given by the equation:

$$R_t = R_{t_0} \left[1 + \frac{dR}{dt} (t - t_0) \right]$$

R_{t_0} = the resistance at a known temperature t_0
 $\frac{dR}{dt}$ = the temperature coefficient of resistance
 t = the temperature at which the resistance
 is sought

For metallic conductors, dR/dt varies between -0.0005 for carbon, and $+0.01$ for magnesium at 600°C . ($1,112^\circ\text{F}$.).

For laboratory and technical use it is more convenient and usually more accurate to employ resistance coils as secondary standards than to construct a primary standard according to the definition given above. Such coils may be purchased, and for work of great accuracy may be sent to the National Bureau of Standards for calibration. The specific resistances of some of the metals and some solutions are shown in Table III.

In order that a current may flow through a conductor it must be impelled by a force; this force is called an electromotive force or potential difference. The commonest unit of force is the *volt*, named after the Italian physicist, Count A. Volta (1745–1827). The international volt is the electromotive force required to maintain a current of 1 amp. through a conductor having a resistance of 1 ohm.

The relation between the current strength, electromotive force, and resistance is shown by Ohm's law, which states that the current strength is directly proportional to the electromotive force and inversely propor-

TABLE III
SPECIFIC RESISTANCE

	Substance	Resistivity, ohm-cm.	Tempera- ture, °C.
Electronic conductors	Aluminum	2.824 × 10 ⁻⁶	20
	Brass	6.4-8.4 × 10 ⁻⁶	20
	Carbon	3,500. × 10 ⁻⁶	20
	Carbon	2,100. × 10 ⁻⁶	1,000
	Copper, annealed	1.7241 × 10 ⁻⁶	20
	Copper, hard-drawn	1.771 × 10 ⁻⁶	20
	Gold	2.44 × 10 ⁻⁶	20
	Graphite	800. × 10 ⁻⁶	20
	Graphite	870. × 10 ⁻⁶	1,000
	Iron, 99.98% Fe	10. × 10 ⁻⁶	20
	Lead	22. × 10 ⁻⁶	20
	Nichrome	100. × 10 ⁻⁶	20
	Platinum	10. × 10 ⁻⁶	20
	Silver	1.59 × 10 ⁻⁶	20
Ionic conductors 25 g. salt in 100 g. solution	Tin	11.5 × 10 ⁻⁶	20
	Zinc	5.8 × 10 ⁻⁶	20
	Acetic acid	658.	18
	Nitric acid	1.30	18
	Potassium hydroxide	1.85	18
	Silver nitrate	9.45	18
	Sodium chloride	4.69	18
	Sodium hydroxide	3.68	18
	Sulphuric acid	1.39	18
	Zinc sulphate	20.8	18

tional to the resistance. This is expressed mathematically by the equation:

$$I = \frac{E}{R} \quad \text{or} \quad E = IR \qquad \begin{matrix} I = \text{amperes} \\ E = \text{volts} \\ R = \text{ohms} \end{matrix}$$

The terms ampere, volt, and ohm as defined in 1893 at the Chicago International Electrical Congress are called the international ampere, volt, and ohm, respectively; they were established as legal units in the United States by Act of Congress in 1894, and are the units in use today.

Direct and Alternating Current. Frequency. A direct current (also called a unidirectional current) is one that always flows in the same direction. It may, however, vary in intensity, may be continuous (non-pulsating) or pulsating. A direct current is used for practically all electrochemical and some electrothermal processes. It is likewise used

to some extent for power, especially street railways service, and also for lighting.

An alternating current is one that reverses its direction periodically; it increases from zero to its maximum strength, then decreases to zero, changes to the opposite direction, increases to a maximum, and returns to zero, thus passing through repeated cycles. The number of cycles per unit of time is called the frequency. The most common frequency in commercial practice is 60 cycles per second, but 25 cycles per second is also used, as, e.g., in the Niagara Falls hydroelectric generating plants. In some applications, as in electric induction furnaces, the frequencies may be as low as 5 cycles per second. The current used for making conductance measurements and that in high-frequency induction furnaces commonly has a frequency of 1,000 cycles per second, while the discharge of a Tesla coil has one of millions of cycles per second.

Coulombs; Coulometers. Of the terms so far discussed the volt represents a pressure factor, and the ampere a current-strength factor. The quantity of electricity is expressed as the product of the current and time. One ampere flowing for 1 second is called a *coulomb*, after the French physicist, C. A. Coulomb (1736–1806). A half ampere flowing

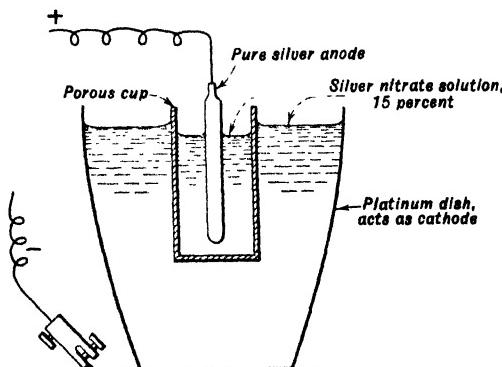


FIG. 3. Silver coulometer.

for 2 seconds or 6 amp. flowing for $\frac{1}{6}$ second would also represent 1 coulomb. Thus:

$$\text{Coulombs} = C = It \quad I = \text{amperes} \\ t = \text{seconds}$$

The quantity of current flowing is measured in a coulometer. One of the most accurate types of coulometers and at the same time the most convenient is the silver coulometer.^{12, 13} It is an electrolysis cell as

¹² T. W. Richards and G. W. Heimrod, *Z. physik. Chem.*, **41**, 302 (1902).

¹³ *Natl. Bur. Standards Bull.*, **10**, 529 (1914); **13**, 479 (1916); *Natl. Bur. Standards Sci. Paper*, **285**, 1916.

TABLE IV
ENERGY CONVERSION FACTORS

To convert from, to multiply by the factor in- dicated at the intersections →	Watt- Hours	Kilowatt- Hours	Kilowatt- Years	Horsepower- Hours	Horsepower- Years	Gram Calories	Kilogram Calories	B.T.U.	Joules
Watt-hours (w-hr.).....	1	0.001	0.11415×10^{-6}	0.001341	0.1531×10^{-6}	860.5	0.8605	3,415	3,600
Kilowatt-hours (kw-hr.).....	1.000	1	0.11415×10^{-3}	1.341	0.1531×10^{-3}	860,500	860.5	3,415	$3,500 \times 10^3$
Kilowatt-years (kw-yr.).....	8.760×10^3	8.760	1	11.747	1.341	7.538×10^6	7.538×10^3	29.9×10^6	31.535×10^6
Horsepower-hrs. (hp-hr.).....	745.7	0.7457	0.0852×10^{-3}	1	0.11415×10^{-3}	641,700	641.7	2,547	$2,684.5 \times 10^3$
Horsepower-yrs. (hp-yr.).....	6.535×10^3	6.535	0.7457	8,760	1	5.621×10^6	5.621×10^3	22.3×10^6	22.53×10^6
Gram calories (cal.).....	1.1625 $\times 10^{-3}$	1.1625 $\times 10^{-6}$	0.1326×10^{-6}	1.558 $\times 10^{-6}$	0.1778×10^{-6}	1	0.001	3.968×10^{-3}	4,183
Kilogram calories (Cal.).....	1.1625	1.1625 $\times 10^{-3}$	0.1326×10^{-6}	1.558 $\times 10^{-3}$	0.1778×10^{-6}	1,000	1	3.968	4,183
British thermal units (B.t.u.)....	0.2928	0.2928 $\times 10^{-3}$	0.0334 $\times 10^{-6}$	0.3929×10^{-3}	0.04483×10^{-6}	252.2	0.2522	1	1,055
Joules.....	277.8×10^{-6}	277.8×10^{-9}	0.3171×10^{-9}	0.3725×10^{-6}	0.04252×10^{-9}	0.2389×10^{-3}	0.9486×10^{-3}	1	

Watts = horsepower $\times 0.001341$.
Horsepower = watts $\times 7,457$.

Joules = amperes \times volts \times seconds.
= watts \times seconds.
= volts \times coulombs.

shown in Fig. 3 having a platinum dish for a container which serves at the same time as cathode. The anode consists of pure electrolytic silver, the electrolyte of a 10 to 20 per cent solution of silver nitrate. The amount of silver deposited is weighed, and the time required to deposit this silver is recorded; from these values the average current strength can be calculated. For less precise work a copper coulometer, Fig. 4, can be used. Such coulometers as the two mentioned above are called weight coulometers. Other types measure the volume of a gas (as hydrogen or oxygen) liberated, and are called volume coulometers. In a third class the change in concentration, or the amount of material liberated at an electrode, is determined by titration; such a coulometer is called a titration coulometer. For a discussion of various types of coulometers the reader is referred to Volume I. Coulometers were formerly called voltameters, and the name still persists; the word coulometer was introduced by Richards and is to be preferred.

Other Electrical Units. The unit of electrical energy is the volt-coulomb or *joule*, named after the English scientist J. P. Joule (1818–1889). The unit of electrical power is the *watt*, named after the Scottish engineer, James Watt (1736–1819). One watt represents 1 joule per second. Some common energy conversion factors are given in Table IV.

CONDUCTANCE

Classes of Conductors. Electrical conductors are of two classes. The first, metallic or electronic conductors, comprises substances in which the current consists of a motion of electrons from one atom to another. Some electrons can move from one atom to another in a metal fairly easily, so that, when a potential difference is applied in a closed circuit, a stream of electrons is produced. As these electrons collide with the atoms of the metal, heat is generated. In all metallic conduction there is a rise of temperature, and a magnetic field is produced around the conductor, but no transfer of ponderable matter takes place. Conduction in carbon and graphite is also of this type.

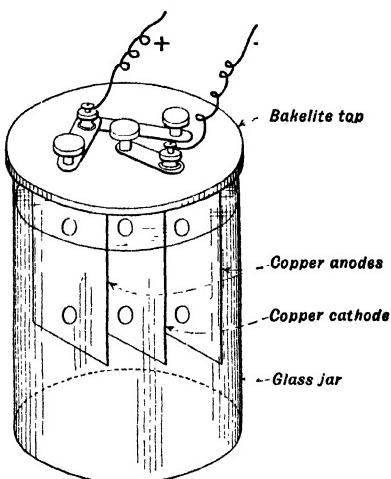


FIG. 4. Copper coulometer.

The second class, electrolytic or ionic conductors, comprises those in which the current consists of a motion of ions, the electrons remaining on their respective ions throughout the conduction. In ionic conduction, as in electronic conduction, a rise in temperature is produced and a magnetic field is set up around the conductor, but in addition matter is transferred. Electrolytic conductors are typified in solutions of acids, bases, and salts, fused salts, some solid salts, and hot gases. Electrolytic conduction always produces chemical change. It is this class of conductors that interests us particularly in this book.

There are also mixed conductors, in which part of the current is carried ionically and part electronically. Such mixed conduction is found in solutions of alkali and alkali-earth metals in liquid ammonia.

Electrolysis Cells. Electrolysis. The solution of the electrolyte or the fused salt is confined in a suitable container. The current is conducted to and from the electrolyte by means of electronic conductors called electrodes. The current enters the electrolyte through the electrode called the *anode*, and leaves it through another called the *cathode*. The container with its electrodes constitutes an electrolysis cell. The passage of a current through the electrolyte is called electrolysis. That part of the electrolyte near the anode is called the *anolyte*; that near the cathode, the *catholyte*.

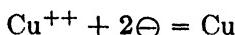
In some electrolytic processes, as in the series system of electro-refining of metals, a number of electrodes are placed in the electrolysis cell between the anode and cathode but not connected to either one by a metallic conductor. The current coming through the electrolyte from the anode enters such an electrode on one side, passes through it, and goes into the electrolyte from the other side. Such an electrode is cathode on one side and anode on the other and is called a *bipolar* or *intermediate electrode*.

When a polar compound is dissolved, positive and negative ions dissociate. In the process of electrolysis, if sufficient voltage is used, all the positive ions move toward the cathode and are called *cations*; all the negative ions move toward the anode and are called *anions*.

Electrochemical Reactions. In the process of electrolysis, chemical changes take place at the electrodes. These changes involve the transfer of electrons and are spoken of as electrochemical changes. The reactions at the anode always involve the surrender of electrons to the external circuit; this is called an oxidation process. At the cathode, electrons are obtained from the external circuit; this is called a reduction process.

In Fig. 5 is shown a diagrammatic sketch of an electrolysis cell in which a solution of copper sulphate is being electrolyzed between two copper electrodes. The nominal "direction of current" is opposite to the

flow of electrons. When a potential difference is applied, electrons in the external circuit move toward the cathode, leave the cathode and fill up the two spaces on the copper ion. It should be remembered that the copper ion is positive because two electrons have left the copper atom and have gone to the SO_4 group; i.e., the copper atom has two more positive charges (protons) within it than it contains electrons. The moment these two lost electrons are replaced by two from the cathode, as in the above reaction, the copper ion becomes an atom of metallic copper, and the copper thus liberated not being soluble is plated on the cathode. This change is represented by the reaction



The symbol \ominus is used to represent an electron. This reaction takes place only with those ions which directly touch the cathode; it is called an electrochemical reaction. The moment the two electrons leave the metallic circuit to discharge the copper ion, two electrons must be supplied from somewhere to attempt to keep up the equilibrium in the electrical system. In this case they are supplied by a copper atom in the anode, directly touching the electrolyte. The copper atom, in giving up two electrons to the circuit, becomes an ion and goes into solution. The electrochemical reaction is represented by



If the cathode consists of some other kind of metallic conductor the reactions are the same; copper goes into solution at the anode, and plates out at the cathode, copper ions constantly moving from the anode toward the cathode.

Faraday's Laws of Electrolysis. One of the first scientists to place electrochemistry on a sound scientific basis was Michael Faraday (1791–1867). In 1833 he formulated two laws, which are called Faraday's laws of electrolysis. The first law expresses the relation between the quantity of electricity passed through an electrolyte and the quantities of substances liberated at the electrodes. The second expresses the relation between the quantities of different substances liberated by the same quantity of electricity. These laws are stated by Creighton in Volume I, as follows: "(1) The quantities of substances set free at the

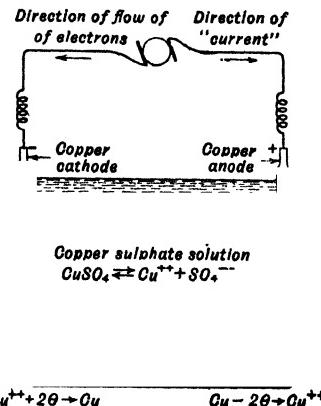


FIG. 5. Electrolysis of a copper sulphate solution between copper electrodes.

electrodes are directly proportional to the quantity of electricity which passes through the solution. (2) The same quantity of electricity sets free the same number of equivalents of substances at the electrodes." According to the first law, if a uniform current flowing for a definite length of time liberates a certain amount of copper, silver, or other substance, doubling the amount of current or doubling the time will double the amount of substance liberated. That is, for any given substance, the amount of change produced by a current is directly proportional to the coulombs passed. According to the second law if the same current passes through a number of cells in series containing copper sulphate, silver nitrate, and potassium chloride, respectively, the amounts of copper, silver, potassium, and chlorine liberated are proportional to their respective equivalent weights.

Faraday. By definition, 1 coulomb of electricity liberates 0.001118 g. of silver from a solution of a silver salt. From this it is a simple matter to calculate how many coulombs are necessary to liberate a gram-equivalent weight of silver, namely, $107.88/0.001118 = 96,494$ coulombs. According to Faraday's second law this same amount of electricity will liberate a gram-equivalent weight of any other material that will separate at the electrodes in an electrolytic solution. This amount of electricity is called a *faraday*; for practical purposes it can be taken as 96,500 coulombs.

$$1 \text{ faraday} = F = 96,500 \text{ coulombs} = 26.8 \text{ amp-hr.} = 1.117 \text{ amp-days}$$

Electrochemical Equivalent. The number of grams of a substance liberated by 1 coulomb of electricity is called the electrochemical equivalent of that substance. The electrochemical equivalent of any substance is therefore $1/96,500$ of its chemical equivalent. This gives a small numerical value; for example, the electrochemical equivalent of divalent copper is 0.0003294 g. Instead, some people prefer to express the electrochemical equivalent in milligrams (0.3294 for Cu^{++}) or in grams per ampere-hour (1.1857 for Cu^{++}). In consulting tables of electrochemical equivalents it is important to note the units used. In Table V are given the electrochemical equivalents of some of the more common elements encountered in electrochemistry.

Current Density. In considering the passage of a current through an electrolyte, the current intensity for any unit of cross-section is a function of the total cross-sectional area and the total current passing through the electrolyte. The current density is the current strength per unit of cross-sectional area. For scientific purposes, current density is commonly expressed as amperes per square decimeter (amp. per sq. dm.); in industrial work the unit in common use is amperes per square foot

(amp. per sq. ft.). In electrochemical work it is generally more important to know the current density at one or both the electrodes (based on the current-carrying part of the electrode immersed in the electrolyte) than current density of the cross-section of the electrolyte. Current densities are therefore commonly expressed as amperes per square foot (or square decimeter) at the anode, or at the cathode.

$$1 \text{ amp. per sq. dm.} = 9.3 \text{ amp. per sq. ft.}$$

Current efficiency is the ratio of the theoretical quantity of current required for a particular reaction to that actually consumed. Faraday's law does not appear to hold for many electrochemical processes as carried out commercially. This is because, in addition to the electrochemical change desired, other changes may also take place, or some of the main product liberated may be lost mechanically or converted in secondary chemical changes; there may also be stray currents registering in the ammeter, but not passing through the electrolyte and the electrodes. If all current is accounted for, it will be found that Faraday's law always holds. Current efficiency can be calculated according to the equation:

$$\begin{aligned} \text{Current efficiency} &= \text{C.E.} = \frac{\text{Theoretical quantity of electricity required}}{\text{Actual quantity of electricity consumed}} \\ &= \frac{\text{Actual amount of product formed}}{\text{Theoretical amount}} \end{aligned}$$

Energy efficiency is the ratio of the theoretical amount of energy required for a particular reaction to that actually consumed. Obviously, the current efficiency is a factor in the energy efficiency. The actual voltage necessary to produce a change, and the theoretical voltage for the change, are also considerations. The theoretical voltage is called the decomposition potential; its magnitude is a function of the concentration of the solution. Decomposition potentials for a number of substances in solution at normal concentration are given in Table VIII. The energy efficiency of an electrolytic process is defined as the ratio:

$$\begin{aligned} \text{Energy efficiency} &= \text{E.E.} = \frac{\text{Theoretical quantity of energy required}}{\text{Actual quantity of energy consumed}} \\ &= \frac{(\text{Decomposition potential}) \times (\text{Current efficiency})}{\text{Actual voltage required}} \end{aligned}$$

Conductance is the reciprocal of resistance, and the unit is the *mho*, also called the *reciprocal ohm*. The specific conductance is the conductance of a material in the form of a cube, the current passing from one face to the opposite one. The common unit is the centimeter-cube,

TABLE V
ELECTROCHEMICAL EQUIVALENTS

(Calculations based on 1 faraday = 96,500 coulombs.)

$Mg.$ per coulomb = $\frac{Eq. wt. \times 1,000}{96,500}$ = Eq. wt. $\times 0.0103627$.	$Amp\text{-hr. per } g. = \frac{96,500}{Eq. wt. \times 3,600}$ = $\frac{26.80555}{Eq. wt.}$
Coulombs per mg. = $\frac{96,500}{Eq. wt. \times 1,000}$ = $\frac{96.5}{Eq. wt.}$	Coulombs per mg. $\times 0.277778$.
Grams per amp-hr. = $\frac{Eq. wt. \times 3,600}{96,500}$ = Eq. wt. $\times 0.0373057$	Lb. per 1,000 amp-hr. = $\frac{96,500 \times 1,000}{Eq. wt. \times 453.59}$ = Eq. wt. $\times 0.082245$.
— Mg. per coulomb $\times 3.6$.	

Element	Sym- bol	Atomic Weight *	Va- lence	Equivalent Weight (Eq. Wt.)	Mg. per Coulomb	Coulombs per Mg.	Grams per Amp-Hr.	Amp-Hr. per G.	Lb. per 1,000 Amp-Hr.	Amp-Hr. per Lb.
Aluminum.....	Al	26.97	3	8.990	0.09316	10.73415	0.33538	2.98171	0.73938	1,352.50
Antimony.....	Sb	121.76	5	24.352	0.25235	3.96271	0.90847	1.10075	2.00283	499.29
			3	40.587	0.42059	2.37761	1.51413	0.66045	3.33808	299.57
Arsenic.....	As	74.91	5	14.982	0.15525	6.44106	0.55891	1.78918	1.23219	811.56
			3	24.970	0.25876	3.86464	0.93152	1.07351	2.05366	496.94
Barium.....	Ba	137.36	2	68.680	0.71171	1.40507	2.56216	0.39030	5.64859	177.04
Beryllium.....	Be	9.02	2	4.510	0.04674	21.39689	0.16825	5.94359	0.37092	2,696.00
Bismuth.....	Bi	209.00	5	41.800	0.43316	2.30861	1.65938	0.64128	3.43784	290.88
			3	69.667	0.72194	1.38516	2.59898	0.38477	5.72976	174.53

— Mg. per mg. $\times 126$.

ELECTROCHEMICAL EQUIVALENTS

25

Boron.....	B	10.82	3	3.607	0.03738	26.75353	0.13456	7.43154	0.29866	3,370.86
Bromine.....	Br	79.916	1	79.916	0.82814	1.20752	2.98132	0.33542	6.57269	152.14
Cadmium.....	Cd	112.41	2	56.205	0.58244	1.71693	2.03677	0.47693	4.62258	216.33
Calcium.....	Ca	40.08	2	20.04	0.20767	4.81537	0.74760	1.33760	1.6482	606.74
Carbon.....	C	12.010	4	3.002	0.03111	32.14523	0.11199	8.92924	0.24690	4,050.30
			2	6.005	0.06223	16.06994	0.22402	4.46588	0.49388	2,024.81
Cerium.....	Ce	140.13	4	35.032	0.36303	2.75462	1.30689	0.76517	2.88121	347.07
		3	46.710	0.48404	2.06594	1.74255	0.57387	3.84166	260.30	
Cesium.....	Cs	132.91	1	132.91	1.37731	0.72606	4.95830	0.20168	10.93118	91.48
Chlorine.....	Cl	35.457	1	35.457	0.36743	2.72161	1.32275	0.75600	2.91626	342.92
Chromium.....	Cr	52.01	6	8.668	0.08982	11.13290	0.32337	3.09247	0.71290	1,402.72
		3	17.337	0.17966	5.56613	0.64677	1.54615	1.42688	701.32	
		2	26.005	0.26948	3.71082	0.97013	1.03078	2.13878	467.56	
Cobalt.....	Co	58.94	3	19.647	0.20360	4.91169	0.75295	1.36436	1.61587	618.86
		2	29.470	0.30539	3.27452	1.09940	0.90959	2.42376	412.58	
Copper.....	Cu	63.57	2	31.785	0.32938	3.03602	1.18576	0.84334	2.61416	382.53
		1	63.570	0.65876	1.51801	2.37152	0.42167	5.22831	191.27	
Fluorine.....	F	19.00	1	19.00	0.19689	5.07895	0.70881	1.41082	1.56266	639.93

* International Atomic Weights, 1941, *J. Am. Chem. Soc.*, 63, following p. 636 (1941).

TABLE V—Continued

Element	Symbol	Atomic Weight *	Vale- lence	Equivalent Weight (Eq. Wt.)	Mg. per Coulomb	Coulombs per Mg.	Grams per Amp-Hr.	Amp-Hr. per G.	Lb. per 1,000 Amp-Hr.	Amp-Hr. per Lb.
Gold.....	Au	197.2	3	65.733	0.68117	1.46806	2.45222	0.40779	5.40621	184.97
			1	197.200	2.04352	0.48935	7.34922	0.13593	16.21871	61.66
Hydrogen.....	H	1.008	1	1.008	0.010446	95.73413	0.03760	26.59284	0.08290	12.063.
Iodine.....	I	126.92	1	126.92	1.31523	0.76032	4.73484	0.21120	10.43854	95.80
Iron.....	Fe	55.85	3	18.617	0.19292	5.18343	0.69452	1.43984	1.53116	653.24
			2	27.925	0.28938	3.45568	1.04176	0.95991	2.29869	435.49
Lead.....	Pb	207.21	4	51.805	0.53684	1.86275	1.93262	0.51743	4.26670	234.70
			2	103.605	1.07363	0.93142	3.86506	0.25877	8.52099	117.36
Lithium.....	Li	6.940	1	6.940	0.071917	13.90490	0.25890	3.86248	0.57078	1,751.99
Magnesium.....	Mg	24.32	2	12.160	0.12601	7.93586	0.45364	2.20441	1.00009	99.90
Manganese.....	Mn	54.93	7	7.847	0.08132	12.29769	0.29274	3.41603	0.64538	1,549.47
			6	9.155	0.09487	10.54069	0.34153	2.92797	0.75295	1,328.11
			4	13.732	0.14230	7.02738	0.51228	1.92205	1.12839	885.43
			2	27.465	0.28462	3.51356	1.02460	0.97599	2.25886	442.70
Mercury.....	Hg	200.61	2	100.305	1.03943	0.96207	3.74195	0.26724	8.24558	121.22
		1	200.610	2.07886	0.48103	7.48390	0.13362	16.49917	60.61	

Molybdenum	Mo	95.95	6	15.992	0.16572	6	0.03427	0.59659	1.67619	1.31526	760.32
		4	23.988	0.24858	4.02284	4	0.89487	1.11746	1.97289	506.88	
		3	31.983	0.33143	3.01722	3	1.19315	0.83812	2.65044	380.17	
Nickel	Ni	58.69	3	19.563	0.20273	4.93278	0.72981	1.37022	1.60896	621.52	
		2	29.345	0.30409	3.28846	1.09474	0.91346	2.41348	414.34		
Nitrogen	N	14.008	5	2.802	0.02904	34.43969	0.10453	9.56778	0.23045	4,339.40	
		3	4.669	0.04838	20.66824	0.17418	5.74079	0.38400	2,604.15		
Oxygen	O	16.0000	2	8.000	0.08290	12.06250	0.29845	3.35070	0.65796	1,519.85	
Palladium	Pd	106.7	4	26.675	0.27642	3.61762	0.99513	1.00490	2.19389	455.81	
		2	53.350	0.55285	1.80881	1.99026	0.50245	4.38777	227.90		
Phosphorus	P	30.98	5	6.196	0.06421	15.55746	0.23115	4.32152	0.50959	1,960.24	
		3	10.327	0.10702	9.33444	0.38526	2.59290	0.84934	1,176.14		
Platinum	Pt	195.23	4	48.8075	0.50578	1.97716	1.82080	0.54921	4.01417	249.12	
		2	97.615	1.01155	0.98858	3.64160	0.27461	8.02835		124.56	
Potassium	K	39.096	1	39.096	0.40514	2.46828	1.45850	0.68563	3.21545	311.00	
Selenium	Se	78.96	6	13.6	0.13637	7.33283	0.49094	2.03690	1.08234	923.92	
		4	19.74	0.20456	4.88855	0.73641	1.35793	1.62352	615.95		
		2	39.48	0.40912	2.44428	1.47283	0.67897	3.24703	307.97		
Silicon	Si	28.06	4	7.015	0.07269	13.75624	0.26170	3.82118	0.57695	1,733.27	

* International Atomic Weights, 1941, *J. Am. Chem. Soc.*, **63**, following p. 636 (1941).

TABLE V—Continued

Element	Symbol	Atomic Weight *	V-a-lence	Equivalent Weight (Eq. Wt.)	Mg. per Coulomb	Coulombs per Mg.	Grams per Amp-Hr.	Amp-Hr. per G.	Lb. per 1,000 Amp-Hr.	Amp-Hr. per Lb.
Silver.....	Ag	107.880	1	107.880	1.11793	0.89451	4.02454	0.24848	8.87259	112.71
Sodium.....	Na	22.997	1	22.997	0.23831	4.19620	0.85792	1.16561	1.89139	528.71
Strontium.....	Sr	87.63	2	43.815	0.45404	2.20244	1.63455	0.61179	3.60347	277.51
Sulphur.....	S	32.06	6	5.343	0.05537	18.06101	0.19932	5.01695	0.43944	2,275.63
Tantalum.....	Ta	180.88	5	36.176	0.37488	2.66751	1.34597	0.74098	2.97530	336.11
Tellurium.....	Te	127.61	6	21.268	0.22039	4.53733	0.79342	1.26037	1.74919	571.69
Tin.....	Tn	118.70	4	29.675	0.30751	3.25190	1.10705	0.90331	2.44062	409.73
Titanium.....	Ti	47.90	4	11.975	0.12410	8.05846	0.44674	2.23846	0.98488	1,015.35
Tungsten.....	W	183.92	6	30.653	0.31765	3.14814	1.14353	0.87449	2.52106	396.66
Vanadium.....	V	50.95	5	10.190	0.10560	9.47007	0.38015	2.63058	0.83808	1,193.20
Zinc.....	Zn	65.38	2	32.690	0.33876	2.95197	1.21952	0.81990	2.68859	371.94

* International Atomic Weights, 1941, J. Am. Chem. Soc., 63, following p. 636 (1941).

but the inch-cube is also in use. Specific conductance is therefore commonly expressed as reciprocal ohms (or mhos) per centimeter-cube (mhos-cm.) or per inch-cube (mhos-in.).

The relation between the specific conductance and temperature is expressed by the following equation:

$$L_t = L_{18}[1 + b(t - 18)] \quad \begin{array}{l} L = \text{specific conductance} \\ t = \text{observed temperature, } ^\circ\text{C.} \end{array}$$

For salts and bases, b varies between 0.02 and 0.025; for acids b varies between 0.01 and 0.016. The conductivity therefore varies between 1 and 2.5 per cent per degree centigrade.

The *equivalent conductance* is the conductance of an electrolytic solution when 1 equivalent of solute is placed between flat parallel electrodes 1 cm. apart. If 1 mole of solute is used instead of an equivalent, the molal conductance is obtained. The equivalent and molal conductance of an electrolyte is a function of the temperature and the concentration (and the solvent, if other than water).

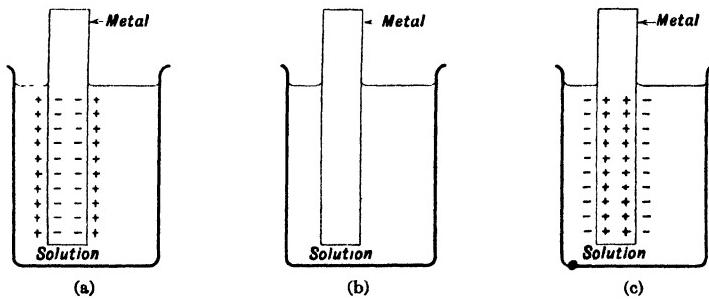
ELECTROMOTIVE FORCE

In the preceding section we were concerned mainly with phenomena in connection with the electric current, disregarding for the time the fact that in order that a current may flow there must be an impelling force. This force, an electromotive force (e.m.f.) expressed as voltage, will be discussed briefly in this section. Using the classical analogy in which electric terms are likened to hydraulic terms, the expression electromotive force may be compared to that of pressure and the term volt to a specific unit of pressure, as pounds per square inch.

Seat of Electromotive Force. When a metal is immersed in water, there is a tendency for the atoms of the metal to become ions and to go into solution, leaving their electrons on the metal, thus giving the metal a negative charge. This tendency is somewhat the same as that of a liquid to assume the gaseous state, and accordingly Nernst¹⁴ has called this pressure the *electrolytic solution pressure*. It cannot be measured directly but is calculated from e.m.f. data. This concept has met with criticism owing to the difficulty of attributing a real physical significance to electrolytic solution pressure. Each metal has its own characteristic electrolytic solution pressure, and the numerical values vary tremendously. For instance, the solution pressure of magnesium is 1.1×10^{43} atmospheres whereas that of platinum is 1×10^{-36} atmosphere. The theory, however, is useful in several ways, especially in obtaining an understanding of how a potential difference is produced in voltaic cells.

¹⁴ W. Nernst, *Z. physik. Chem.*, 4, 150 (1889).

When a metal dips into a solution of its own ions, as zinc in a zinc sulphate solution or silver in a silver nitrate solution, there is, in addition to the electrolytic solution pressure, another force called osmotic pressure which tends to force the ions from solution onto the metal surface, and thereby give the metal a positive charge. There are, then, two opposing forces: the electrolytic solution pressure forcing ions into the solution, the ions leaving their electrons behind and thereby giving the metal a negative charge; and osmotic pressure forcing the ions onto the metal and thereby giving the metal a positive charge.



The electrolytic solution pressure exceeds the osmotic pressure and the metal is charged negatively, as when zinc dips into a zinc sulphate solution.
The electrolytic solution pressure equals the osmotic pressure and there is no potential difference between the metal and the solution.
The osmotic pressure exceeds the electrolytic solution pressure and the metal is charged positively, as when copper dips into a copper sulphate solution.

FIG. 6. Charges on metals.

With metals like magnesium and zinc and others toward the electro-negative end of the electromotive series as listed in Table VII, the electrolytic solution pressure exceeds the osmotic pressure, and the charge of the metal when dipping into a solution of its own ions is negative. With metals toward the positive end of the series, the reverse is true; the osmotic pressure exceeds the electrolytic solution pressure and the metal receives a positive charge. Figure 6 illustrates three examples of metals dipping into solutions of their respective ions. In (a) the metal is charged negatively; i.e., the electrolytic solution pressure exceeds the osmotic pressure. In (b), there is no potential difference between the metal and the solution; the electrolytic solution pressure equals the osmotic pressure. In (c) the metal is charged positively; the osmotic pressure exceeds the electrolytic solution pressure.

Single-Electrode Potential. When an electrode (usually a metallic conductor) dips into a solution containing its own ions, as shown in Fig. 6, a potential difference is set up between the electrode and the solution. This is called the single-electrode potential. This potential cannot be measured directly, for there is no completed circuit. If an

attempt is made to complete the circuit there will always result a second electrode dipping into the same solution or into another solution in contact with the first one. Therefore, when measurements are made of single-electrode potentials the result is the composite of at least two separate potentials. Such a combination is called a cell; and each half,

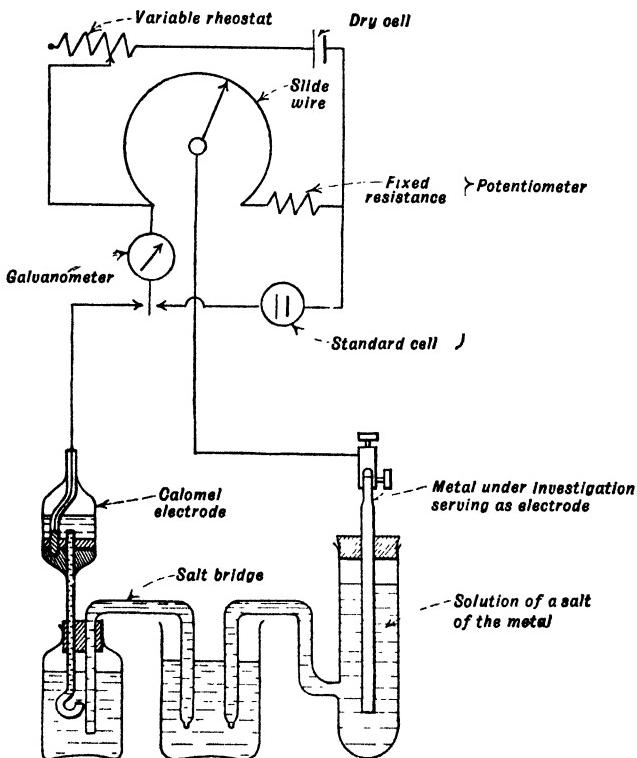


FIG. 7. Measurement of single-electrode potentials.

consisting of an electrode dipping into a suitable solution, is called a half-cell or half-element, and also, very commonly, simply an electrode. Several different kinds of half-cells have been adopted as standard for making such measurements; they are called reference cells, or more commonly reference electrodes. These will be discussed in a later section of this chapter.

In Fig. 7 is illustrated the set-up for measuring single-electrode potentials.¹⁵ It consists of a calomel electrode as the reference electrode; this

¹⁵ For more detailed description see Creighton, Vol. I; and F. Daniels, J. H. Mathews, and J. W. Williams, *Experimental Physical Chemistry*, McGraw-Hill Book Company, New York, 1941.

constitutes one of the half-cells. The other half-cell consists of the metal under investigation dipping into a solution of its ions of known concentration. Each half-cell has a suitable side arm dipping into a common intermediate solution contained in a beaker. The solution in the beaker is called a "salt bridge"; it may consist of a potassium chloride or ammonium nitrate solution. The salt bridge serves to minimize the potential difference at the solution-solution junctions and sometimes also to prevent precipitation of the solutions. The potential difference at the solution-solution junction has a maximum of about 0.035 volt, and by means of a suitable salt bridge it may be reduced almost to insignificance.

The combination described above constitutes a voltaic cell; its voltage can be measured with a potentiometer as indicated in the illustration. The voltage reading obtained will be the algebraic difference between the voltage of the metal in the solution of its ions and that of the calomel electrode. The voltages of the solution-solution junctions also affect the voltage reading, but the latter is usually considered as zero, though equations have been developed for calculating this potential.¹⁶ To simplify matters, the voltage of the calomel electrode may arbitrarily be called zero, so that the voltage reading obtained on the potentiometer gives directly the single-electrode potential of the metal.

The actual potential difference between an electrode and a solution (i.e., the single-electrode potential of a metal) depends upon: (1) the electrode material, (2) the nature of the ions in the solution, (3) the concentration of the ions, (4) the temperature, and (5) the pressure (which applies particularly to gas electrodes). In addition, the numerical value obtained in measuring this potential will be dependent on the kind of reference electrode used.

Calculating Single-Electrode Potentials. For an equilibrium of the type

$$M^{n+} = M - n\ominus \quad (1)$$

Nernst developed the following equation:

$$nEF = RT \ln \frac{P}{P'} \quad (2)$$

n = valence of the metal ion
 E = single-electrode potential at the equilibrium under consideration
 F = faraday = 96,500 coulombs
 R = the gas constant = 8.32 joules
 T = absolute temperature, Kelvin scale
 p = osmotic pressure of the metal ions
 P = electrolytic solution pressure of the metal

¹⁶ G. N. Lewis and L. W. Sargent, *J. Am. Chem. Soc.*, **31**, 363 (1909). For references to other equations see Creighton, Vol. I; Mathews, Daniels, and Williams, *op. cit.*

This equation can also be written in the form

$$E = \frac{RT}{nF} \ln \frac{P}{P'} \quad (3)$$

In order to put the equation into a form so that it can be handled more easily, it can be assumed that, for dilute solutions of strong electrolytes, osmotic pressure is directly proportional to the concentration. Then $P' = kC$, where C is the concentration of the metallic¹⁷ ions in gram-ions per liter of solution, and k is a constant. Equation 3 then becomes:

$$E = \frac{RT}{nF} \ln \frac{k}{P} + \frac{RT}{nF} \ln C \quad \begin{matrix} k = \text{a constant} \\ C = \text{concentration of the metal ions} \\ \text{in gram-ions per liter} \end{matrix} \quad (4)$$

For any pure metal, the term $\frac{RT}{nF} \ln \frac{k}{P}$ is a constant at any given temperature, and it is called the normal electrode potential, E_0 . Equation 4 then becomes

$$E = E_0 + \frac{RT}{nF} \ln C \quad (5)$$

or converting from natural to common logarithms, the equation becomes:

$$E = E_0 + \frac{2.3026RT}{nF} \log_{10} C \quad (6)$$

for 18° C., $\frac{2.3026RT}{F} = 0.0577$; for 25° C., 0.0591; for room temperature the value 0.058 is generally taken, and so equation 6 can be written

$$E = E_0 + \frac{0.058}{n} \log_{10} C \quad (7)$$

For calculating normal electrode potentials the equation is rewritten

$$E_0 = E - \frac{0.058}{n} \log_{10} C \quad (8)$$

E is the voltage as obtained by direct measurement as would be obtained from the set-up shown in Fig. 7. This is done at some convenient known metal salt concentration. For this, C , the number of gram ions per 100 g. of solvent, can be approximated by dividing the equivalent conductance of the salt at the concentration used by the equivalent con-

¹⁷ "Hydrogen ions" can be substituted for "metallic ions."

ductance at infinite dilution. These equivalent conductance values can be obtained for a number of salts from various references.¹⁸

Reference Electrodes. In the preceding section it was mentioned that the calomel electrode may serve as a reference electrode; several other electrodes may be used for that purpose. The characteristics of all such electrodes should be reproducibility, constancy of voltage, and a low but definitely established temperature coefficient. Such reference electrodes or half-elements are also called standard electrodes by some writers.

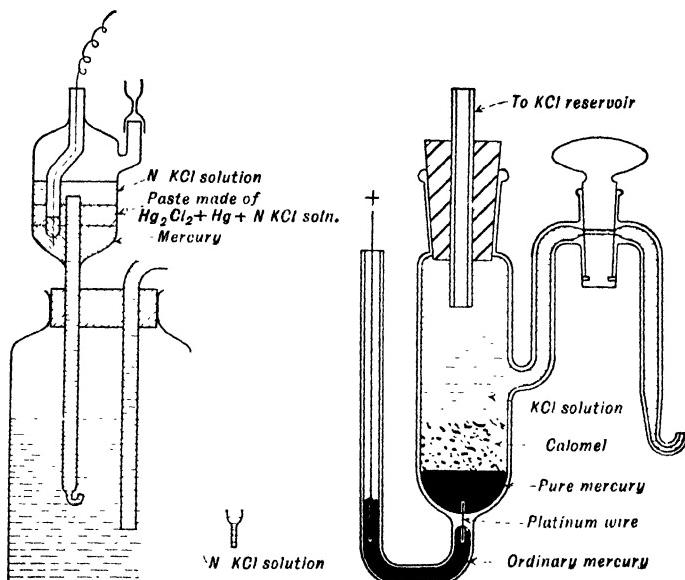


FIG. 8. Two types of calomel half-cells.

Figure 8 shows two different forms of calomel electrodes. In both, the bottom of the main electrode chamber contains mercury; into this dips a glass tube with a closed end and fused platinum point to make connection between the mercury and the exterior of the cell. Placed over the mercury is a layer of paste made by grinding together calomel, Hg_2Cl_2 , a little mercury, and a potassium chloride solution. The potassium chloride solution has the same concentration as the potassium chloride solution above it, which may be either normal, deci-normal, or saturated. There are then the three different calomel electrodes: the normal, the deci-normal, and the saturated calomel electrode. Each

¹⁸ Landolt-Bornstein, *Physikalisch-Chemische Tabellen*, Berlin. C. D. Hodgman, ed., *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, Cleveland.

has its characteristic voltage and temperature coefficient as shown in Table VI.

TABLE VI
REFERENCE ELECTRODE POTENTIALS

Half-Cell	Scheme	Electrode Potentials, 25° C.			Equations for Calculating Absolute Voltages (E) at Various Temperatures, °C. (t)
		Hydrogen electrode = zero	Normal calomel electrode = zero	Absolute voltage	
Deci-normal calomel electrode	Hg-Hg ₂ Cl ₂ 0.1 N KCl	+0.3376	+0.0588	+0.6236	$E = 0.618 + 0.0008(t - 18)$ volt
Normal calomel electrode	Hg-Hg ₂ Cl ₂ N KCl	+0.2848	0.0000	+0.5648	$E = 0.5606 + 0.0006(t - 18)$ volt
Saturated calomel electrode	Hg-Hg ₂ Cl ₂ Sat. KCl	+0.2458	-0.0382	+0.5266	$E = 0.5266 + 0.0002(t - 25)$ volt
Hydrogen electrode	Hg N H ⁺	0.0000	-0.2822	+0.2826	

NOTE: Electrode potentials have not been determined with uniform agreement. For example, the voltages given in current literature for the N calomel electrode (hydrogen electrode = zero) vary from 0.280 to 0.2881 at 25° C. The values given above are used commonly, but there are discrepancies when comparing one column with another. The values for absolute voltages are especially uncertain.

Another reference electrode in considerable use is the hydrogen electrode, illustrated in Fig. 9. It consists of a piece of platinum wire (or foil) sealed through the end of a glass tube. A little mercury is placed in the bottom of the tube for easy electrical connection. Around this tube is placed another one supplied with a side arm through which pure hydrogen is introduced. The platinum wire must be coated with finely divided platinum which is saturated with hydrogen. This is accomplished by cleaning the wire by dipping it into warm *aqua regia*; the electrode is then rinsed and placed as cathode in a 1 per cent solution of platinic chloride and electrolyzed for several minutes with an e.m.f. of about 3 volts (two dry cells in series) using another platinum wire as anode. By this process the platinum wire is coated with finely divided platinum called platinum black and the electrode is said to be "platinized." The electrodes are then placed in a beaker containing distilled water and a drop of concentrated sulphuric acid, and the electrolysis is continued in order to saturate the platinum black with hydrogen. The platinized platinum electrode must be placed in distilled water until used and must be replatinized from time to time. The hydrogen may be purified by passing it through a solution of alkaline pyrogallol, then through a solution of potassium permanganate, and finally washing with

water. For use, the electrode is dipped into an acid solution, normal with respect to hydrogen ions. A 2 *N* sulphuric acid solution is almost exactly normal with respect to hydrogen ions.

A number of other reference electrodes are in use, notable among which

is the quinhydrone electrode. The quinhydrone and the glass electrodes are described in Chapter XIV.

Attempts have been made to determine the absolute potential difference between the electrodes and the solution of reference electrodes by combining them with other half-cells that have no potential difference, so that the combined voltage of the cell is actually that of the one half-cell only. An electrode having no potential difference at the metal-solution junction is called a null electrode. One type of null electrode consists of a copper electrode dipping into a solution containing potassium cyanide and copper sulphate of proper concentration. Another type is the dropping electrode. A stream of small drops of mercury falls from an orifice through a solution of *N* potassium chloride containing a small amount of calomel, Hg_2Cl_2 . However, there is still a question

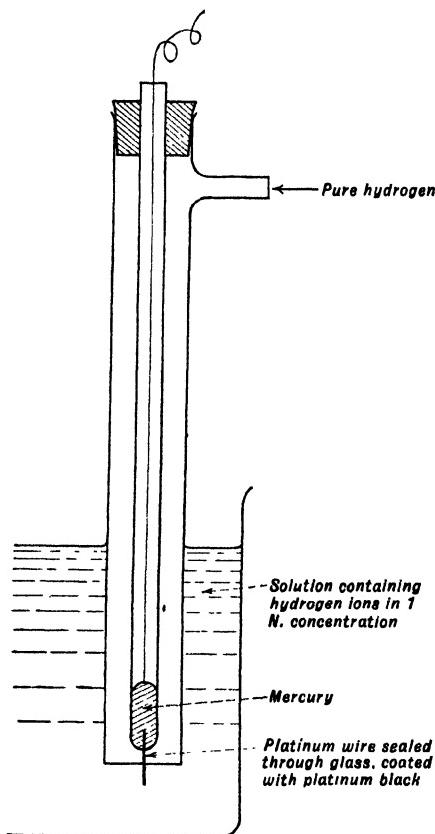


FIG. 9. A hydrogen electrode.

of the reliability of absolute electrode potentials, and therefore electrolytic potentials are usually reported as based on the hydrogen electrode as zero.

Normal Electrode Potential. The electrode potentials of a number of metals can be determined by direct measurement as explained in a previous section. Since, however, the voltage depends upon a number of factors, the conditions under which the measurements are made should be standardized as much as possible in order that the electrode potential of one metal may be comparable with that of another. The metals can then be listed in order from the most negative to the most positive, which will be the order of the familiar electromotive series as

given in Table VII. The measurements are generally made at 18° or 25° C., the metals dipping into a solution containing its own ions in molal concentration. Such voltages are called in the literature by various names—which has caused confusion—such as electrolytic potentials, characteristic electrode potentials, molal electrode potentials, and, very commonly, normal electrode potentials.

In making the determination, the reference electrode is generally the calomel or the hydrogen electrode, but if the calomel electrode is used, the voltages can be calculated in terms of the hydrogen electrode as zero by adding algebraically + 0.2828 to the readings obtained on the basis of the normal calomel electrode as zero.

Confusion has arisen in the past as to the algebraic sign of the potentials, but the sign as given in Table VII with zinc as negative has been quite generally adopted internationally except that the *International Critical Tables* list the signs reversed, with zinc positive. Some of the earlier literature also lists zinc positive, and it behooves the reader to note particularly the convention used.¹⁹

The Electromotive Series. The electrolytic potentials as listed in Table VII are in the order of the electromotive force series of the metals. This series is of considerable aid in the study of chemistry in general, but specifically in electrochemistry.

A metal will replace another metal below it in the series. A piece of iron dipped into a copper sulphate solution will become coated with copper. The iron takes the place of the copper in the solution, and an equivalent amount of copper plates out on the iron. When all the iron has been coated with copper, further action is stopped. Likewise, zinc will replace iron in solution, and nickel will replace copper. For instance, a nickel anode placed accidentally in an acid copper-plating solution will become coated with copper when no current is passing. This phenomenon is referred to as deposition by immersion, and contact plating.

Under the same rule it is possible to tell in a general way whether or not an acid will dissolve a metal. Metals above hydrogen in the series will replace the hydrogen of the acid and form a salt. On the other hand, metals below hydrogen will not be attacked by an acid, unless the action is an oxidation. Copper and silver are not attacked by hydrochloric acid. But nitric acid and hot concentrated sulphuric acid will attack most of the metals, the action being one of oxidation if the metal is below hydrogen in the series.

The elements at the upper end of the electromotive series are very active chemically; those at the lower end are quite inert. For instance,

¹⁹ For a more complete discussion of the signs of electrode potentials, see Creighton, Vol. I, p. 193.

TABLE VII
ELECTROLYTIC POTENTIALS AT 25° C.

Referred to hydrogen as zero. The sign is that of the charge on the electrode.

Cations		Anions	
Li, Li ⁺	-2.96 volts	S, S ⁻⁻	-0.51
K, K ⁺	-2.92	O ₂ , OH ⁻	+0.40
Na, Na ⁺	-2.72	I ₂ , I ⁻	+0.54
Ca, Ca ⁺⁺	-2.5	Br ₂ , Br ⁻	+1.07
Mg, Mg ⁺⁺	-1.87	Cl ₂ , Cl ⁻	+1.36
Al, Al ⁺⁺⁺	-1.35		
Zn, Zn ⁺⁺	-0.76		
Cr, Cr ⁺⁺	-0.6		
Cr, Cr ⁺⁺⁺	-0.5		
Fe, Fe ⁺⁺	-0.44		
Cd, Cd ⁺⁺	-0.40		
Co, Co ⁺⁺	-0.29		
Ni, Ni ⁺⁺	-0.22		
Sn, Sn ⁺⁺	-0.14		
Pb, Pb ⁺⁺	-0.13		
Fe, Fe ⁺⁺⁺⁺	-0.04		
H ₂ , 2H ⁺	0.00		
Sb, Sb ⁺⁺⁺	+0.1		
Cu, Cu ⁺⁺	+0.34		
Cu, Cu ⁺	+0.52		
2Hg, Hg ₂ ⁺⁺	+0.7986		
Ag, Ag ⁺	+0.7995		
Pd, Pd ⁺⁺	+0.82		
Hg, Hg ⁺⁺	+0.86		
Au, Au ⁺⁺⁺	+1.3		

water will combine with sodium and potassium, but *aqua regia* is required to dissolve gold. Therefore, the metals toward the upper end of the series are never found free in nature—their active character has given them sufficient opportunity to combine with other elements; but gold, platinum, and even copper are found native.

For the same reason, the compounds containing elements at the upper end of the series are quite stable. The oxides of the metals down to manganese cannot be completely reduced even in a current of hydrogen, whereas the oxides of silver, mercury, gold, and platinum can be reduced by heating in the atmosphere. Likewise, corrosion of the metals toward the upper end of the series takes place quite readily. All the metals above copper rust fairly easily in the atmosphere, but metals below copper do not rust.

In choosing metals for a voltaic cell, the farther the metals are apart in the series, the greater the voltage of the cell. If each metal dips into

a solution of its own ions in normal concentration, the voltage of the cell is the algebraic difference between their electrolytic potentials. It is not practicable to select metals from opposite ends of the series for the construction of voltaic cells. The most electronegative metal that it is practicable to use is zinc, and that, with one minor exception, is used in all voltaic cells. Copper or carbon are commonly used for positive poles. Obviously, carbon is not listed in the electromotive force series because it does not form ions.

If several ions exist together in an electrolytic solution in a cell, and the voltage is gradually raised from zero, the first metal to plate out is the lowest one in the series, provided that the ionic concentrations of the several metals are equivalent. As the voltage is increased, the metals plate out progressively toward the top of the series. This explains why it is possible to plate metals below hydrogen in the series, from acid solutions, without the evolution of hydrogen, whereas care must be used in plating metals that are above hydrogen in the series, from such solutions. This fact is also the basis for the separation of two or more metals by electrodeposition.

Decreasing the concentration of the metallic or the hydrogen ions in solution makes their electrolytic potentials more negative. For this reason it is possible to plate nickel from a weak acid solution, for the relatively high nickel-ion concentration makes the potential of the nickel more positive than that of the dilute hydrogen ions, and nickel will plate out unless an excessively high current density is used by applying too high a voltage. By employing complex ions in cyanide solutions in silver and gold plating it is possible to make the concentration of the silver ions so low that the potential becomes more negative and thus approaches that of iron, greatly reducing the difficulty due to deposition by immersion.

Voltaic Cells. When a metal dips into a solution of its ions, as, for instance, when a bar of zinc dips into a zinc sulphate solution, the process of atoms each leaving two electrons behind and going into solution as ions does not proceed indefinitely. In fact, the process is checked so quickly that the amount of zinc going into solution cannot be determined analytically. This is because the electrostatic attraction of the opposite charges almost instantly stops the process of zinc going into solution as ions. The same is true of a bar of copper dipping into a copper sulphate solution; the transfer of Cu^{++} ions from the solution to the metal is arrested from proceeding indefinitely by the electrostatic attraction of the opposing charges. In both instances, equilibrium conditions are attained almost instantly.

If, however, the electrons on the zinc metal are removed continuously,

equilibrium is not attained and zinc will continuously pass into solution as ions. Likewise, in the case of the copper, if from some outside source electrons are supplied to the copper to neutralize the Cu^{++} ions on the metal, equilibrium is not attained and copper continues to deposit on the metal from the ions in solution.

Both processes can be brought about by connecting the copper and zinc electrodes with a metallic conductor, such as a piece of wire, and by bringing the zinc sulphate and copper sulphate solutions into intimate contact with each other. This contact can be arranged by dividing a glass jar into two compartments by a porous diaphragm and placing the two solutions on opposite sides, or by placing the heavier copper sulphate solution in the bottom of the jar and carefully pouring the zinc sulphate solution on the top of this. The electrons from the zinc electrode pass along the wire to the copper electrode and there neutralize the Cu^{++} ions on the metal. In this manner, equilibrium is not attained at either electrode, with the result that zinc goes into solution and copper plates out, and the passage of the electrons along the wire from one electrode to the other produces an electric current. This illustrates the action of a voltaic cell; the one described is the Daniell cell.

The magnitude of the single-electrode potential of each of the above electrodes depends upon the difference in magnitude between the osmotic pressures, p_{Zn} , p_{Cu} , of the ions in the solution and the electrolytic solution pressures, P_{Zn} , P_{Cu} , of the corresponding metals. If $P > p$, the potential is negative; if $P < p$, the potential is positive. In this particular example $P_{\text{Zn}} > p_{\text{Zn}}$ and $P_{\text{Cu}} < p_{\text{Cu}}$. To obtain the maximum potential difference between the two electrodes, it is necessary to bring the value of p_{Zn} to its lowest amount, and to bring the value for p_{Cu} to its maximum. Since the osmotic pressure of the ions increases with concentration, these two conditions can be obtained by making the concentration of the zinc sulphate solution very dilute, and by saturating the copper sulphate solution.

This can be stated in another way although the principle involved is the same. When a metal dips into a solution of its own ions the electrode potential becomes more negative on the decrease of the metal-ion concentration, and more positive on its increase. Since zinc is the negative electrode, it can be made negative to its maximum value by placing it in a dilute solution of Zn^{++} ions, or better still, by having no Zn^{++} ions in the solution. Therefore, in some type of cells, when new, the zinc electrode dips into a sulphuric acid or magnesium sulphate solution, for there must be some conducting material. When such a cell is used, zinc goes into solution, p_{Zn} and the potential of the zinc electrode increase, and therefore that of the whole cell drops. At the copper electrode it is

desirable to keep the Cu^{++} -ion concentration and therefore p_{Cu} high; this can easily be accomplished by keeping an excess of copper sulphate crystals in the solution around the electrode.

It is interesting to note in this connection that by reversing the condition of the metallic-ion concentrations the polarity of the cell can be reversed. If the concentration of the zinc sulphate around the zinc electrode is increased (thereby increasing the concentration of the Zn^{++} ions), and if the concentration of the Cu^{++} ions is decreased gradually by adding potassium cyanide, KCN , to the copper sulphate solution, the voltage of the cell gradually decreases to zero and finally reverses polarity.

In the discussion above, the Daniell cell was taken as a concrete example. Similar descriptions would hold for other cell combinations.

Polarization. When a current is passed through an electrolysis cell, the voltage of the cell terminals is raised above its static value. If two smooth platinum electrodes are immersed in a sulphuric acid solution and a potential difference is applied, beginning with zero voltage and gradually increasing, it will be found that as long as the voltage is below 1.70 volts no current will continue to flow. It is true that, at any voltage below this value, a current will flow for a short time but will soon cease. This is because oxygen liberated on the anode and hydrogen on the cathode produce a counter e.m.f., and, if the impressed voltage across the terminals of the cell is less than 1.70 volts, the counter e.m.f. created by the oxygen-hydrogen cell will equal the impressed voltage after a short time and stop further flow of current. Above 1.70 volts the oxygen and hydrogen liberated start to leave their respective electrodes; their concentrations therefore do not increase; and the maximum of the voltage that they generate has been exceeded. The equilibrium potential of the hydrogen-oxygen cell is 1.23 volts. The difference between this theoretical or equilibrium voltage and the 1.70 volts actually needed to make a current pass through the cell is called the polarization voltage.

Likewise, when a voltaic cell discharges a current, the voltage across the cell terminals drops below the equilibrium value. The difference between the equilibrium voltage and the actual voltage delivered by a voltaic cell is called the polarization voltage.

Polarization is of great importance in industrial electrochemistry. It increases the voltage required in the operation of electrolysis cells and decreases the voltage obtained from voltaic cells. It explains why the energy efficiency of a storage battery is less than the current efficiency. A storage battery may be considered an electrolysis cell during charge and a voltaic cell during discharge. During charge the polarization raises the required voltage above the equilibrium voltage of the cell;

during discharge, polarization causes the voltage to drop below the equilibrium voltage.

Conditions Necessary for the Production of Voltaic Cells. In order to produce a voltaic cell, it is necessary to have two electrodes; each electrode must dip into an electrolyte, and, if the two dip into different electrolytes, the electrolytes must be in contact with each other. The following combinations may produce voltaic cells and may also produce polarization in electrolysis cells or in the voltaic cells themselves.

1. Two unlike electrodes dipping into the same electrolyte. The bichromate, dry, and storage cells are examples of voltaic cells produced by this combination. It is not necessary that the two electrodes be composed of different chemical materials. A carbon and a graphite electrode, or an unstrained and a strained iron²⁰ electrode, will produce a potential difference. It is also a common condition causing polarization. If two iron electrodes dip into a copper sulphate solution, there is no polarization. On the passage of a current, however, copper plates on the cathode and it acts like a copper electrode. The iron and copper electrodes in the copper sulphate solution produce a counter e.m.f., or polarization.

2. Two like electrodes dipping into the same electrolyte but at different temperatures. This is of no importance as a means of producing voltaic cells and of but small importance in polarization in electrolysis cells.

3. Two like electrodes dipping into the same electrolyte but at different ionic concentrations. This again is of no importance as a means of producing a voltaic cell but it produces the well-known concentration polarization in electrolysis cells and in lead-acid storage cells. This type of polarization can be overcome in electrolysis cells by stirring the solution.

4. Two like electrodes dipping into unlike electrolytes. This combination is of little practical importance, although it is used in one method for gold electroplating, the so-called "salt-water" plating described in Chapter VI.

5. Two electrodes of like materials but at different pressures dipping into the same electrolyte. This applies especially to gas and to mercury²¹ electrodes.

6. Two like electrodes placed in the same electrolyte, but one placed above the other.²²

7. Combinations of the above, as exemplified in the Daniell cell.

²⁰ W. H. Walker and C. Dill, *Trans. Am. Electrochem. Soc.*, **11**, 153 (1907).

²¹ Th. Des Coudres, *Wied. Ann.*, **46**, 292 (1892).

²² R. R. Ramsey, *Phys. Rev.*, **18**, 1 (1901).

Depolarizers. When a current passes through a cell, be it an electrolysis or a voltaic cell, its passage produces conditions that cause polarization. If the current density is very low, the polarization is negligible in some cells as it is in the standard Weston cell. In others, polarization is a factor of considerable importance. A substance that overcomes or reduces polarization is called a depolarizer.

In primary cells, the liberation of hydrogen on the cathode is an important form of polarization; therefore the depolarizer must be a substance that will oxidize the hydrogen to water. Depolarizers may be solid or liquid; liquid depolarizers act more rapidly than solid ones, but they tend to diffuse to the anode and attack it unless the diffusion is checked. This can be done with the aid of a diaphragm, which, in the Grove-Bunsen cell, is a porous cup surrounding the cathode and containing the depolarizer. A diaphragm increases the resistance of a cell and complicates its construction. A solid depolarizer should react rapidly with the discharged hydrogen, must make good contact with the cathode, and should have a low electrical resistance. The resistance can be decreased by the addition of carbon or other inert conducting material.

Concentration polarization is present in all primary cells and in storage cells, but in primary cells it is usually overshadowed by polarization due to the liberation of hydrogen. No depolarizer is used to counteract concentration polarization, but the cells can be designed originally to reduce differences in concentration at the anode and cathode by permitting diffusion of the electrolyte to take place as rapidly as possible. In electrolysis cells concentration polarization can be reduced by agitation of the electrolyte.

Decomposition Potential. The decomposition potential of a substance in solution is the potential difference which is just sufficient to cause continuous electrolysis to take place. If the resistance of the electrolyte is considered negligible and if there is no polarization, the decomposition potential of a solution of normal ion concentration is slightly greater than the sum of the electrolytic potentials of the cation and anion, respectively. (See Table VII, p. 38.) Since the individual electrode potential and the resistance of the electrolyte are both functions of the concentration and of the temperature of the electrolyte, it follows that the decomposition potential also is a function of the concentration and temperature of the electrolyte. The decomposition potentials of a number of electrolytes in solution are given in Table VIII;²³ the decomposition potentials of a number of fused electrolytes, in Table IX.²⁴

²³ M. Le Blanc, *Z. physik. Chem.*, **8**, 299 (1891).

²⁴ B. Neumann and E. Bergve, *ibid.*, **21**, 152, 160 (1915).

TABLE VIII
DECOMPOSITION POTENTIALS OF ELECTROLYTES
Normal solutions between platinum electrodes

Electrolyte	Decomposition Potential, Volts	Electrolyte	Decomposition Potential, Volts
Cadmium sulphate	2.03	Silver nitrate	0.70
Calcium chloride	1.89	Sodium carbonate	1.71
Cobalt sulphate	1.92	Sodium chloride	1.98*
Cobalt chloride	1.78	Sodium sulphate	2.21
Copper sulphate	0.80	Potassium hydroxide	1.67
Lead nitrate	1.52	Sodium hydroxide	1.69
Lithium chloride	1.86	Zinc sulphate	2.55
Nickel sulphate	2.09	Ammonium hydroxide	1.74
Nickel chloride	1.85	Sulphuric acid	1.67
Potassium carbonate	1.74	Nitric acid	1.69
Potassium sulphate	2.20	Phosphoric acid	1.70
Potassium chloride	1.96	Acetic acid	1.57
Silver sulphate	0.80	Oxalic acid	0.95

* In electrolytic chlorine-caustic manufacture at the concentration of the sodium chloride solution used, the decomposition potential of sodium chloride is taken as 2.3 volts.

TABLE IX
COMPOSITION POTENTIALS OF FUSED ELECTROLYTES

Electrolyte	Temperature, °C.	Decomposition Potential, Volts
Barium chloride	650	3.05
Calcium chloride	585	2.85
Lithium chloride	800	2.39
Potassium chloride	800	2.8
Potassium hydroxide	200	2.4
Potassium hydroxide	530	1.8
Sodium chloride	800	2.65
Sodium hydroxide	180	2.38
Sodium hydroxide	280	2.25
Sodium hydroxide	640	1.32
Sodium sulphate	890	2.5

Decomposition potentials may be determined in several ways. In one method an electrolysis cell is prepared containing the compound under investigation in solution. Both electrodes are of platinum, and an electromotive force known to be below the decomposition potential is applied. The voltage is gradually increased; below a voltage corresponding

to the decomposition potential there is but a slight increase in the current through the cell, but at the point of the decomposition potential the current increases abruptly with increase in applied voltage, and beyond this point is proportional to the applied electromotive force. The curve obtained from plotting voltage against current has the general shape of the overvoltage curve shown in Fig. 10. The point of inflection of the

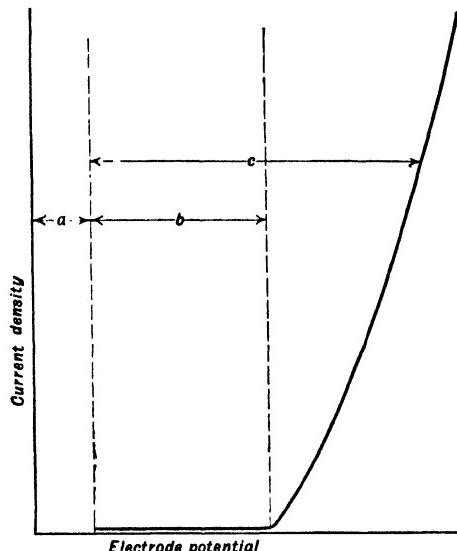


FIG. 10. Overvoltage curve.

a = equilibrium potential.

b = overvoltage at start of electrolysis.

c = overvoltage at higher current density.

curve corresponds to the decomposition potential of the material under investigation.

In another method for determining decomposition potentials the same type of electrolysis cell is used but an electromotive force above the decomposition potential is supplied and electrolysis is allowed to proceed for several minutes. The circuit is then broken and the voltage across the terminals of the cell is read at once. This voltage reading is the decomposition potential of the compound under investigation.

Overvoltage. When an attempt is made to liberate a gas on an electrode there is generally some polarization, even at low current densities; at high current densities this polarization may become of considerable magnitude. The polarization that is obtained when just enough voltage is applied to evolve a gas at an electrode is the overvoltage of that gas on

the given electrode material under the conditions of operation. It is the difference between equilibrium potential of the gas under the given conditions and the potential required to cause evolution of the gas on that electrode. In Fig. 10 is shown a typical overvoltage curve of hydrogen on a metal.

In industrial electrochemistry we are largely interested in the hydrogen overvoltage on various metals. Hydrogen is evolved on a platinum black electrode at practically its equilibrium potential, and so the overvoltage of hydrogen on a metal is sometimes defined as the difference in the potential required to evolve hydrogen on that metal and that required to evolve it on platinum black. Since the minimum voltage required to liberate hydrogen with suitable electrodes is about 1.1 volts, the overvoltage with any given pair of electrodes is the difference between the actual voltage required and 1.1 volts.²⁵

O vervoltage depends upon a large number of factors, some of which are not fully understood; frequently it is difficult to duplicate results, so that a variety of values are found in the literature. Table X gives the overvoltage of hydrogen on various metals according to some investigators.

The following factors affect the overvoltage²⁶ of hydrogen on metals:

1. Increase in current density increases the overvoltage. The overvoltage-current density curves on the various metals investigated seem to approach 1.3 volts as a maximum.
2. Increase in temperature decreases the overvoltage, although the overvoltage of hydrogen on platinized-platinum is practically independent of the temperature.
3. Increase in pressure generally decreases the overvoltage.
4. O vervoltage increases with time, but in some cases the maximum overvoltage is reached almost instantly.
5. Superimposing an alternating current on a direct current lowers the overvoltage.

Just as there is a hydrogen overvoltage on a cathode material, there are also oxygen overvoltages on an anode material as shown in Table XI,²⁷ and chlorine overvoltage on various materials, that on graphite, as determined by the same investigators, being shown in Table XII.²⁸

²⁵ R. Glazebrook, *A Dictionary of Applied Physics*. II. *Electricity*, pp. 60-61, The Macmillan Company, New York, 1922.

²⁶ M. Knobel and associates, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923); **44**, 443 (1923).

²⁷ M. Knobel, P. Caplan, and M. Eiseman, *Trans. Am. Electrochem. Soc.*, **43**, 70 (1923).

²⁸ *Ibid.*, p. 68.

TABLE X
HYDROGEN OVERVOLTAGES

Group in the Periodic Table	Metal	Overvoltage *		
		Knobel †	Newberry ‡	Creighton §
I	Sodium		Volts	Volts
	Copper	0.80	0.33	0.35
	Silver	0.88	0.29	
	Gold	0.59	0.36	
II	Magnesium			Volts
	Zinc	1.06	0.75	0.70
	Cadmium	1.22		
	Mercury	1.07+	0.53	
III	Aluminum	1.00	0.19	0.50
	Thallium			
IV	Carbon	0.89	0.39	0.45
	Graphite	0.98	0.35	
	Tin	1.22	0.49	
	Lead	1.18	0.42	
V	Antimony		0.43	0.42
	Tantalum			
	Bismuth	1.14	0.42	
VI	Chromium			0.32
	Molybdenum			
	Tungsten		0.27	
VII	Manganese			0.25
VIII	Iron	0.82		0.18
	Nickel	1.05	0.24	
	Rhodium			
	Iridium			
	Palladium	0.70		
	Platinum (platinized)	0.04		
	Platinum (smooth)	0.29	0.12	

* For additional values, see W. A. Caspary, *Z. physik. Chem.*, **30**, 89 (1899); J. Tafel, *ibid.*, **50**, 641 (1905); A. Thiel, et al., *Z. anorg. Chem.*, **83**, 329 (1913); **132**, 15 (1923).

† Ten amperes per square decimeter, 25° C., 2 N H₂SO₄. M. Knobel, P. Caplan, and M. Eiseman, *Trans. Am. Electrochem. Soc.*, **43**, 64-67 (1923).

‡ Ten amperes per square decimeter, 15° C., N H₂SO₄. E. Newberry, *J. Chem. Soc.*, **109**, 1051-66 (1916).

§ Vol. I.

TABLE XI

OXYGEN OVERRVOLTAGES

Current density, 1.0 amp. per sq. dm.

Temperature, 25° C. Electrolyte, *N* KOH solution.

Material	Overvoltage, volts
Soft graphite	0.896
Gold	0.963
Copper	0.580
Silver	0.729
Chemmetal	1.02
Smooth platinum	0.85
Platinized platinum	0.521
Smooth nickel	0.519
Spongy nickel	0.563

TABLE XII

CHLORINE OVERRVOLTAGE ON GRAPHITE

Temperature, 25° C.

Current Density, amp. per sq. dm.	Overvoltage, volts
4	0.186
7	0.193
10	0.251
20	0.298
50	0.417
74	0.466
98	0.489
113	0.535

Overvoltage is of considerable industrial importance. For instance by referring to the electrolytic potentials, Table VII, page 38, it would appear that zinc could not be plated from an acid solution, for the hydrogen ions would be expected to plate out in preference to the zinc ions. This, however, is not the fact, for the overvoltage of hydrogen on zinc, added to the equilibrium potential of hydrogen, is sufficient to bring the voltage necessary to plate hydrogen on zinc above the potential of zinc plating. Overvoltage necessitates the expenditure of increased energy in electrolytic processes involving the liberation of gases. Thus, in some cases the overvoltage necessary to liberate a gas is increased threefold when the current density is increased tenfold.

Confusion exists in the literature regarding the meaning of the terms *polarization* and *overvoltage*. As applied to gas evolution, *overvoltage* has

two distinct meanings, each of which has minor variations. These two meanings are expressed as follows in the A.S.A. definitions²⁹ originally proposed:

1. "Overtoltage of a gas upon a specified electrode is the polarization involved in the evolution of that gas on that electrode at a specified current density."

2. "Overtoltage of a gas on a specified electrode is the minimum polarization at which visible gas evolution occurs, or at which there is a marked increase in current density."

Commenting on these definitions, Blum and Vinal³⁰ state: "Both of these definitions are used in the literature, sometimes with no clear distinction. The first definition is most commonly employed, and is necessarily involved or implied in such statements as 'the effect of current density on overvoltage.' The preference given to it in the printed A.S.A. list reflects its present greater usage. Strictly speaking, however, there is no more reason for using a distinct word to describe gas polarization than to define metal polarization. Every meaning conveyed by overvoltage in that sense can be expressed as well or better in terms of polarization."

Blum and Vinal recommend that the term *overvoltage* be used to designate the minimum polarization at which a particular reaction occurs at an appreciable rate on a specified electrode, or at which, with a small increase in voltage, there is a marked increase in current density.

Standard Cells. Several types of voltaic cells have been developed that have each a definite reproducible voltage and are called standard cells. The number of standard cells that have been proposed is large, but those in general use are few. The characteristics of a good standard cell are constancy of voltage, reproducibility, and a low but definitely established temperature coefficient.

One of the leading and most commonly used standard cells is the Weston cadmium normal cell, shown in Fig. 11. It is made of a sealed H-shaped glass container. The lower ends are supplied with sealed-in platinum wires for electrical connection. The positive electrode contains pure mercury at the bottom, on the top of which is placed a layer of paste consisting of mercurous sulphate, Hg_2SO_4 , and a small quantity of cadmium sulphate, $CdSO_4$. The bottom of the negative electrode contains a cadmium amalgam containing 12.5 per cent of cadmium. The remainder of each leg is then filled with large crystals of cadmium

²⁹ American Standards Association, "Report on Proposed American Standard Definitions of Electrical Terms." Printed by the American Institute of Electrical Engineers, August, 1932.

³⁰ W. Blum and G. W. Vinal, *Trans. Electrochem. Soc.*, 66, 359 (1934).

sulphate, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, to a height such that about half of the cross-bar of the H is filled. The remaining part of the cell is then filled with a saturated solution of cadmium sulphate and the upper ends of the tubes are sealed, allowing sufficient air space for thermal expansion. The voltage of the cell has been internationally accepted as

$$E = 1.0183 \pm 0.0001 \text{ volt at } 20^\circ \text{ C.}$$

The temperature coefficient is small, and a lengthy formula has been developed for calculating the voltage for different temperatures. The

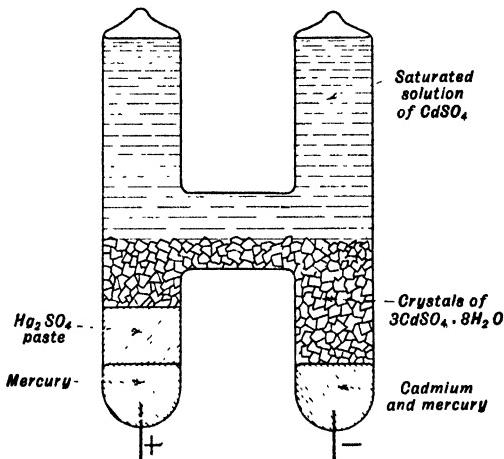


FIG. 11. Weston cadmium normal cell.

following abbreviated expression, however, is sufficiently accurate for most purposes:

$$E_t = E_{20} - 0.0000406(t - 20)$$

The Clark cell is constructed similarly to the Weston cell except that zinc amalgam replaces the cadmium amalgam, the paste above the mercury in the positive pole consists of mercurous sulphate and zinc sulphate, the remainder of the cell being filled with a zinc sulphate solution. The voltage of the cell at 15° C. is 1.4328.

Standard cells find wide and useful application in the determination of unknown voltages, as that of voltaic cells and thermocouples.

Passivity. If a piece of iron with a fresh metallic surface is dipped into a concentrated nitric acid solution, there will be no chemical action on the fresh surface. The iron is said to have become passive, and the phenomenon is known as passivity. If the iron is taken from the acid and rinsed, the passivity is not removed; if it is then dipped into a solution of copper sulphate, there will be no deposition of copper.

Passivity is observed in a number of metals when used as anodes in electrolytic processes; this is particularly true when the anodic reaction is one involving the liberation of oxygen. In the electroplating of nickel in a nickel sulphate solution, a point is reached as the current density is increased at which evolution of oxygen is obtained instead of solution of nickel. As the current density is again reduced the solution of nickel will recommence but it may not do so immediately.

For metals of the iron group, the current density required to bring about a passive state depends to a large extent upon the anion present. The following anions are listed in order³¹ of increased current density required to produce passivity: OH⁻, IO₃⁻, BrO₃⁻, ClO₃⁻, CrO₄²⁻, NO₃⁻, CH₃COO⁻, SO₄²⁻, Cl⁻. It will be observed that those ions which are of a strongly oxidizing nature promote passivity, and a high current density is required to produce passivity of an anode in a solution containing Cl⁻ ions. This explains why in the literature on nickel plating one frequently finds the statement that nickel chloride is added to some nickel solutions to increase anode corrosion. Obviously hydrochloric acid would serve the same purpose, but this would also increase the hydrogen-ion concentration which is objectionable in nickel plating.

Passivity is observed to about like degrees for iron, cobalt, and nickel. Passivity of chromium has received considerable study, and it presents a situation somewhat peculiar. As the current density is increased to the point at which metal solution ceases, passivity manifests itself not as oxygen evolution but metal solution as Cr⁶⁺ which occurs at a lower potential than the former.

Gold shows marked passivity even in chloride solution. In a neutral gold chloride, AuCl₃, solution, gold dissolves anodically at a potential of +1.1 to 1.2 volts³² according to the equation Au - 3 \ominus = Au⁺⁺⁺. At 1.4 volts the anode becomes passive suddenly, and at 1.73 volts chlorine is evolved.

The behavior of platinum and allied metals as insoluble anodes is so common that it is not always realized that this is a case of passivity.³³

It has been observed by Adler³⁴ and others that in some cases a current density can be obtained at which passivation and activation can occur alternately as a periodic phenomenon.

³¹ E. P. Schoch, *Trans. Faraday Soc.*, **9**, 275 (1913).

³² A. Coehn and C. L. Jacobsen, *Z. anorg. Chem.*, **55**, 321 (1907).

³³ A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, p. 140, Edward Arnold and Company, London, 1924. Pages 137 to 142 give a more complete discussion on the subject of passivity than can be undertaken in this book.

³⁴ A. Adler, *Z. physik. Chem.*, **80**, 385 (1912).

CHAPTER III

PRIMARY CELLS

In the early experiments in electrochemistry the only sources of electrical energy were discharges from electrostatic machines. The basic discoveries (1756) leading to the development of the primary cell, the electrolysis of water (1789), and the discovery of the different potentials of the metals, as well as the concept of the electromotive series (1794), antedated the advent of the primary cell.¹ However, up to that time only very small quantities of electricity were available, and it is for this reason that the voltaic cell proved such an important factor in the development of electrochemistry. All of Davy's work in electrochemistry, such as the isolation of potassium, sodium, barium, strontium, and magnesium, was done with current from primary cells, as was also the classical work by Faraday; but with the development of the dynamo and the storage battery the primary cell has played a less important part in the field of electrochemistry. Primary cells, however, find wide application on account of their convenience. They are used in flashlights; for operation of electric bells, signal systems, telephones, radios; and for ignition of internal-combustion engines, to mention some of the leading applications.

In primary cells, chemical energy is converted into electrical energy with a reduction in the free energy of the system. It is desirable that this loss in free energy manifests itself entirely as electrical energy outside the cell, but this ideal is never attained in practice, because the internal resistance of a cell is not zero and the reactions within the cell are never completely reversible. At the anode the evolution of oxygen is avoided by the use of a soluble metal as anode, but passivity of the anode if present will produce irreversibility. Care in the selection of anode material and of electrolyte will reduce passivity to small proportions. If the cathode reaction consists of the discharge of a metallic ion on a metal, the process is very nearly reversible; but if the reaction at the cathode involves the discharge of H^+ , polarization will be present so that an appreciable overvoltage may be required for the discharge of the H^+ ,

¹ As late as 1797 it was reported that 14,600 discharges of a static machine were required to produce $\frac{1}{2}$ cu. in. of gas.

which will reduce the voltage of the cell. Suitable depolarizers will help to eliminate this overvoltage. Concentration polarization, although also a factor, is less important. The internal resistance of the cell can be kept low by avoiding diaphragms, by placing the electrodes close together, and by using an electrolyte of high conductivity. The subject of depolarizers was discussed in the preceding chapter.

Voltaic cells are those in which chemical changes produce electrical energy, in distinction to electrolysis cells in which electrical energy from an outside source produces chemical changes within the cell. The type of unit which cannot conveniently be recharged, which usually is dis-

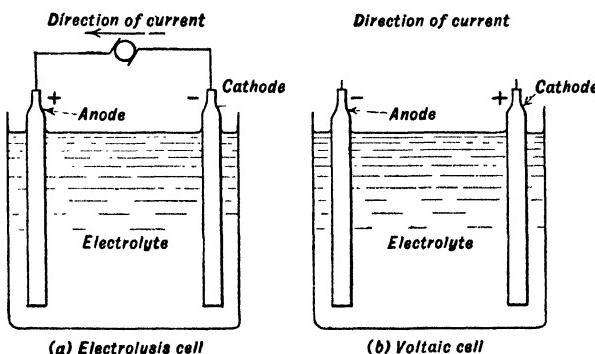


FIG. 12. Terminology used in connection with electrolysis cells and voltaic cells.

carded after a single exhaustion of its component elements, or which requires replacement of its exhausted chemical constituents to bring it back to its original condition, is considered a primary cell and is the type discussed in this chapter. In the next chapter will be taken up another class of voltaic cells, namely, those cells in which the exhausted cell is brought to its state of charge by the passage of an electric current from an outside source through the cell in the reverse direction of the discharge current. Such cells are called secondary or storage cells.

A battery consists of a number of voltaic cells, whether primary or secondary, connected electrically so that they act as one unit.

Nomenclature. In an electrolysis cell, the current enters at the positive pole and leaves at the negative pole; the positive pole is called the anode, and the negative pole the cathode. In a primary cell, the current also leaves at the cathode and enters at the anode, but the cathode is called positive and the anode negative. In an electrolysis cell, then, the current flows from the positive electrode to the negative electrode within the cell; in a primary cell it flows from the positive electrode, or pole, to the negative pole outside of the cell. This is illustrated diagrammatically in Fig. 12.

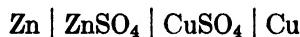
EARLIER CELLS

Volta's Cell. In about 1800 Volta constructed the first primary cell of which there is any record.² It consisted of pairs of copper and zinc discs one above the other, each pair separated by a piece of cloth moistened with a solution of common salt. The electrode reactions are



The hydrogen liberated at the cathode clings to the cathode as fine bubbles; this hydrogen is the cause of a drop in the voltage of the cell for two reasons: (1) the gaseous hydrogen has a high resistance; and, more important, (2) the hydrogen acts as an electrode so that the combination, zinc | acid | H₂, develops a voltage but of a smaller magnitude than the cell originally had. This second, reverse voltage is called a back e.m.f., encounter e.m.f., or polarization. If the cell is then allowed to stand idle for a time, the hydrogen gradually escapes and the original voltage of the cell is restored; the cell is then said to have recovered.

Daniell Cell and Gravity Cell. The Daniell cell was developed in 1836, and with its later modifications was for a time the most common type of primary cell. It consists of a zinc anode dipping into a dilute solution of zinc sulphate, sulphuric acid, or magnesium sulphate, and a copper cathode dipping into a solution of copper sulphate, the two electrolytes being in intimate contact. The cell consists of the system



The electrode reactions are:



The voltage of the cell is given by the equation

$$E = 1.1 + 0.029 \log \frac{(\text{Cu}^{++})}{(\text{Zn}^{++})} \text{ volts}$$

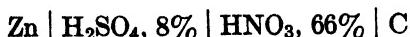
where $\frac{(\text{Cu}^{++})}{(\text{Zn}^{++})}$ is the ratio of the copper and zinc ions in their respective solutions. It is therefore desirable to have a high copper-ion and low zinc-ion concentration. The cell will gradually have a drop in the voltage as the zinc ions accumulate owing to solution of the anode. The

² George Gamow, *The Birth and Death of the Sun*, Macmillan and Co., Ltd., London, 1941, illustrates in Fig. 7 what is called an ancient Persian electric battery, probably of the first century B.C.

zinc anode is attacked chemically and only about 30 per cent of the zinc is utilized electrochemically.³

In the original form, the cell contained a porous cup which held the zinc sulphate and zinc anode, and surrounding this was a saturated solution of copper sulphate, containing the copper cathode. In a later modification of this cell, the copper cathode is placed horizontally in the bottom of a glass jar, as shown in Fig. 13, and is covered with a solution of saturated copper sulphate. On top of this is carefully poured a lighter solution of zinc sulphate or of magnesium sulphate. The two solutions are kept from mixing by the difference in their densities, and this modification is called a gravity cell. The zinc anode is placed horizontally in the upper part of the sulphuric acid solution. The copper cathode is covered with copper sulphate crystals in order to insure the maximum voltage. Since the zinc electrode is shaped to suggest a crow's foot, the cell is also called a crow-foot cell. The voltage of the cell is about 1.18 volts at the start, but gradually falls down to 1.12 volts as the zinc ions become more concentrated in the anolyte. When the cell stands on open circuit, copper ions will gradually diffuse toward the anode and will completely cover the anode with copper. To avoid this the cell must not stand on open circuit but must be kept on low current drain when not in use by circuit closure through a high resistance. The migration of the copper ions toward the cathode then prevents their diffusion to the zinc anode.

Grove-Bunsen Cell. In 1839 Grove devised a primary cell consisting in part of a zinc anode dipping in an electrolyte consisting of 8 per cent sulphuric acid. The cathode consisted of platinum in the Grove cell, which Bunsen later changed to retort carbon. The electrode reactions are the same as in Volta's cell. Grove, however, surrounded the cathode with a porous cup containing 66 per cent nitric acid. The acid oxidizes the liberated hydrogen and thus prevents its collection on the cathode; it therefore reduces and even eliminates polarization. Such an agent is called a depolarizer. The cell system is:



The liquid junction in the walls of the porous cup where the two electrolytes meet also produces a voltage, but, as at most liquid-liquid

³ F. Haber, *Grundriss der technischen Electrochemie*, R. Oldenbourg, Leipzig, 1898.

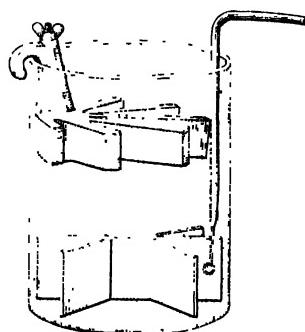
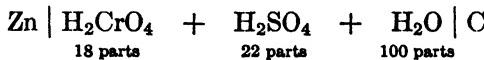


FIG. 13. Gravity cell.

junctions, the potential difference is so small that it can be neglected in a practical consideration. The voltage of the cell ranges from 1.8 to 1.96, according as the concentration of the nitric acid ranges from 45 per cent to fuming acid. The resistance of the cell is low, but the cell liberates unpleasant nitrous fumes. The cells were usually constructed so that the zinc anode could be withdrawn from the electrolyte to eliminate corrosion during periods of idleness.

Bichromate Cell. The bichromate cell of Poggendorf consists of the system:



The electrode reactions can be represented as follows:



The chromic acid acts as a depolarizer, the hydrogen being oxidized to water; the action, however, is not very rapid, and the cell polarizes fairly rapidly unless a soluble chloride is added which acts as a catalyst. There is also a concentration polarization due to an accumulation about and in the pores of the carbon cathode of Cr^{+++} ions and an impoverishment of $\text{Cr}_2\text{O}_7^{--}$ ions. On standing, the concentration of the ions tends to become uniform, and the cell recovers. The voltage of the cell is high, about 2 volts, but on account of its polarization it is particularly suited for intermittent use only. The electrolyte is made from sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, and sulphuric acid, which interact to form chromic acid. It was customary to provide means for removing the zinc from the electrolyte when the battery was not in use.

Leclanché Cell. The Leclanché cell⁴ developed in 1865 consists of a zinc anode, a carbon cathode, an electrolytic solution of about 20 per cent ammonium chloride, and a manganese dioxide depolarizer, so that the cell system is $\text{Zn} \mid \text{NH}_4\text{Cl} \mid \text{MnO}_2 + \text{C}$. The carbon rod may be placed in a porous cup surrounded by manganese dioxide and granular carbon well compacted to give intimate contact, or as is more common in the later ones, the granular carbon and manganese dioxide are mixed with a binder and molded into a hollow cylindrical form and the zinc anode is mounted centrally. The open-circuit e.m.f. of the cell is about 1.5 volts, but on the discharge of a heavy current it may drop to near 1 volt. The Leclanché cell is suited chiefly for intermittent service.

Some of the above cells are still in use, especially the gravity cell, but their commercial importance in the United States is practically nil.⁵

⁴ E. Friederich, *Elektrochem. Z.*, **16**, 219, 252, 287 (1909-10).

⁵ For a discussion of the various types of batteries that have been developed in the past, the reader is referred to some early books on batteries, such as A. Niaudet,

They have largely given way to the modern dry cell and the alkaline primary cell.

PRESENT-DAY CELLS

Dry Cells. The present-day dry cell is the product of development of the Leclanché cell. By adding absorbing material for the electrolyte it developed (1885) into the so-called dry cell, which first made its appearance in the United States about 1890. The dry cell consists of a zinc anode and a carbon cathode, with zinc chloride and ammonium chloride solution as electrolyte. The cell system, therefore, is

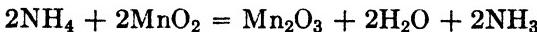


and the electrode reactions are:



In the conventional dry cell, a zinc container serves as anode; and placed concentrically in it, but not touching the zinc bottom, is a carbon cathode.

The carbon electrode is surrounded by manganese dioxide, MnO_2 , which acts as a depolarizer by oxidizing the hydrogen, which may be represented by the equation:



With the ZnCl_2 normally present in the cell the reaction proceeds to the diammino salt, $\text{ZnCl}_2 \cdot 2\text{NH}_3$. In order to decrease the resistance of the dioxide, carbon or graphite is mixed with it. In addition to the above-mentioned fundamental materials are a number of accessory materials.

Raw Materials and Their Functions. *Zinc.* For electrochemical reasons, zinc, because it is the anode, should be of high purity, but it must also possess high mechanical strength. For the larger types of cell the zinc is used in thicknesses of 0.035 to 0.050 cm. (0.014 to 0.020 in.).

Carbon. The carbon cathode really serves as a collector of the current, for the carbon-manganese dioxide mixture is part of the cathode; since the manganese dioxide has a very high resistance, the carbon mixed with it is the greater part of the active cathode, but the manganese dioxide must be considered as an energy-producing electrode of definite cathodic potential. The cathode is usually in the form of a cylindrical rod.

Electric Batteries, translated by L. M. Fishback, John Wiley & Sons, New York, 1893. W. R. Cooper, *Primary Batteries*, The Electrician Printing and Publishing Company, London, 1901; second edition, 1916. More recent books are by W. Guntherschulze, *Galvanische Elemente*, Wm. Knapp, Halle, Germany, 1929; A. M. Codd, *Practical Primary Cells*, Sir Isaac Pitman and Sons, London, 1929; C. Drucker and A. Finkelstein, *Galvanische Elemente und Akkumulatoren*, Akad. Verlags. mbH., Leipzig, Germany, 1932.

Petroleum coke is used for making the rod. The rod extends above the seal and is provided with a binding screw.

Manganese Dioxide. Manganese dioxide acts as a depolarizer to oxidize the liberated hydrogen; it must therefore be selected with its suitability for that purpose in mind, but the kinds and amounts of impurities present must also receive consideration. Manganese dioxide occurs native as the ore, pyrolusite. It is obtained from Montana, Caucasia, Africa, Cuba, Puerto Rico, Java, Brazil, and Japan. The ores from these sources all differ in their depolarizing powers, and this difference is independent of the MnO_2 content. Of the impurities, Fe_2O_3 and the lower oxides of manganese, MnO , Mn_2O_3 , Mn_3O_4 , are harmless up to about 4 per cent. Metallic iron accidentally mixed in the ore is very injurious, and all ore should be passed over magnetic separators. Copper, lead, and silver in any soluble forms are active poisons, for they plate out on the zinc anode, thereby producing local couples and causing short cell life. These metals should be present only in amounts under 0.02 per cent. Montana manganese dioxide is commonly used. Artificial manganese dioxide is used to a considerable extent in European practice and also in America for special heavy-duty cells.

Graphite. Graphite is added to the manganese dioxide to reduce the resistance of the cell. Artificial (Acheson) graphite has been in common use but considerable amounts of acetylene black are now also used in the battery mix.

Sal ammoniac, ammonium chloride, NH_4Cl , is the main electrolyte material. The commercial grade, in the form of a white dry powder, is suitable. Sal ammoniac of American manufacture is the best grade obtainable and is used exclusively.

Zinc chloride, $ZnCl_2$, enters into the cell reaction as previously noted and reduces local action at the zinc anode, and in so doing prolongs the life of the cell. As is true of sal ammoniac, the best grades are produced in this country.

Mercuric chloride, $HgCl_2$, is added in small amounts, dissolved in the electrolyte, for the purpose of slightly amalgamating the inside surface of the zinc can, in order to reduce corrosion. It also raises the voltage slightly. In European practice, the zinc cans are amalgamated directly before they are filled.

Liners. The manganese dioxide-graphite mixture must be kept from making direct contact with the zinc container. One means, common in America for the No. 6 cells, is to place a pulpboard liner between the zinc and the mixture. In place of this, the carbon cathode with its surrounding mixture may be placed in a cotton bag, in such a manner that the top part of the carbon is free. This method is much used for

flashlight cells. It is common American practice, however, to make cells especially of flashlight size in which neither pulpboard liner nor muslin wrapping is used, as shown in Fig. 14. In this type the paste acts as a separator.

Paste. A narrow annular space between the liner and the zinc can is filled with a paste containing some of the electrolyte materials. One of the best pastes is made from wheat flour, similar to that used for

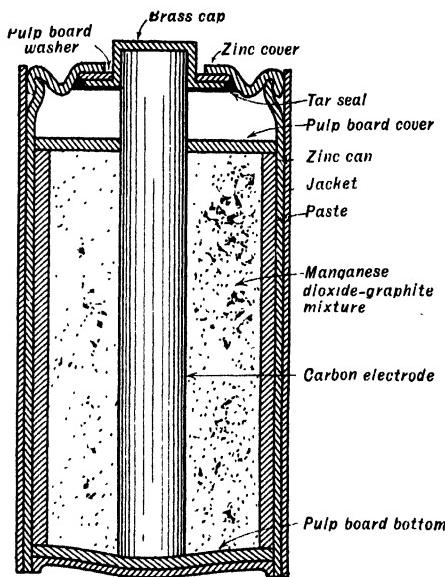


FIG. 14. A flashlight cell in section.

household purposes. Potato starch is often added in the ratio of about 1 to 2.

The outside of the cell is protected by a pasteboard jacket, and the top of the cell is sealed with a metal top.

The electromotive force of a dry cell is between 1.5 and 1.6 volts. The amperage of a 6-in. dry cell on short circuit through an ammeter ranges from 18 to 25 amp., but this method of testing dry cells is not a true indication of their qualities for comparing two or more different brands of cells. The normal capacity of a 6-in. dry cell is of the order of 35 amp-hr., that of a No. 950 flashlight cell about 4 amp-hr., for normal operating conditions.

Dry cells deteriorate on standing, and several methods are used to increase their shelf-life. This deterioration is due to local action, caused by impurities more electropositive than zinc, which plate out on the inner surface of the zinc container wherever they are near the zinc metal.

In such cases exposed zinc near such a plated metal acts as anode and the more electropositive metal as cathode; the metal of the can supplies the short circuit; and the electrolyte of the cell serves as the electrolyte of the local couple. In the continuous discharge of such local couples, the zinc goes into solution and hydrogen is plated out on the other metal. Fortunately, the overvoltage of hydrogen on these cathodic areas is higher than the voltage of the couple, and the action is arrested. In other cases, polarization reduces the local action, or the action may form insoluble products which incrust the surface. Even in the absence of impurities, inequalities in the structure of the zinc may cause local action. Zinc chloride is added to the mixture placed in the cell to reduce this action. Mercury, either introduced as an amalgam in the can, or added as mercuric chloride and then precipitated on the zinc, also reduces the local action. The effect of the mercury is twofold. It makes the inner surface of the can more uniform, and therefore reduces differences which are necessary for the two poles of a local couple, and the high overvoltage of hydrogen on the amalgamated surface tends to reduce local action.

Another method formerly used to increase shelf-life was to ship the cells bone-dry; such cells are called desiccated cells; water must be added to them before they are put into use. In another type of cell, all the electrolyte and paste were included, deterioration being avoided by omitting the zinc can, which was inserted when the cell was desired for use. Reserve-type cells enjoyed some importance, but the general improvement of standard grades, especially as regards their keeping quality, has gradually led to abandonment of reserve cells.⁶

The larger dry cells were formerly made in five sizes, numbered 4 to 8 inclusively, the numbers corresponding to the height of the cells in inches. The No. 6 is the only one now produced by most manufacturers. In addition there are well over a dozen sizes of flashlight cells, and these are assembled into a large number of different arrangements of batteries.

The rapid growth of popularity of portable radio sets has created a demand for a compact "B" battery. When 30 round can-type cells are used to make a conventional 45-volt battery, less than 60 per cent of the total volume of the assembly is productive space. A flat type of battery has been developed which is a reversion in principle of the original Volta pile. A carbon plate is placed horizontally, and on top of this is a flat cake made of a mixture of carbon and manganese dioxide dampened with electrolyte. Placed above this is a paper liner impregnated with electrolyte, and on top of this is a zinc plate. Another carbon plate is placed above this, and then the other ingredients in the same order as

⁶ For a thorough study of the physical-chemical aspects of the Leclanché dry cell see Farrington Daniels, *Trans. Electrochem. Soc.*, **53**, 45-64 (1928).

before to produce another cell; this is continued until a battery of desired voltage is obtained. The whole is then encased in a suitable container with the two end plates of the series of cells making contact with external connectors. Great attention has been given toward reduction of non-productive space,⁷ and units are now available in the "Eveready Mini-Max" cell in which over 95 per cent of the total volume of the unit is productive space.

Other Types of Dry Cells. There are several other types of dry cells, but of very minor importance.⁸ In the so-called silver chloride cells, the electrodes are made of zinc and silver, with silver chloride placed around the silver electrode to act as a depolarizer. One size is $2\frac{3}{8}$ in. high and $\frac{3}{4}$ in. in diameter; the top is sealed with plaster of Paris. The open-circuit voltage is 1, and the short-circuit current is $\frac{1}{2}$ amp. A peculiar characteristic of this type of cell is that the open-circuit voltage and short-circuit current both rise after some current has been drawn from the cell; after the cell has been allowed to stand idle for a time both drop off to some extent.

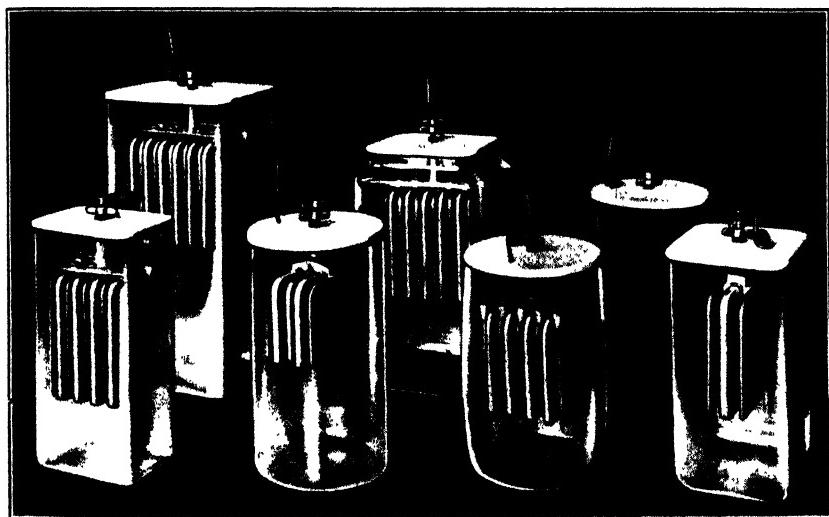


FIG. 15. An assortment of alkaline primary cells.

Alkaline Primary Cells. A primary cell of considerable importance is the Lalande type, represented in the United States by the Edison unit, shown in Fig. 15, and also by the Waterbury and Columbia types. The negative electrode consists of amalgamated zinc; the positive pole of

⁷ H. F. French, *Proc. Inst. Radio Engrs.*, **29**, 299 (1941).

⁸ "Electrical Characteristics and Testing of Dry Cells," *U. S. Bur. Standards Circ.* **79**, 1919.

copper oxide, CuO, which gradually is converted to metallic copper. In one form, the positive plates are made from copper scale; the scale is roasted to oxidize it completely and is then ground and mixed with a temporary binder and pressed into cakes a little larger than the finished electrode will be. The cakes are dried and baked at a red heat; this decomposes the binder and leaves the mass of copper oxide porous. After cooling, the copper oxide at the surface of the electrode is reduced to metallic copper by zinc dust or by other methods to make it conducting. The zinc plates have in their lower portions small panels of varying

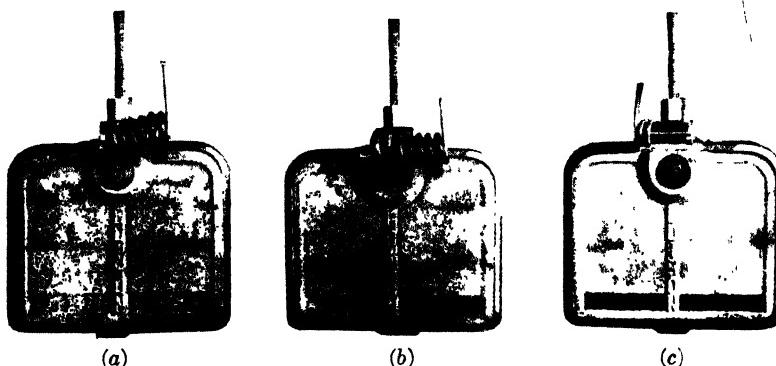


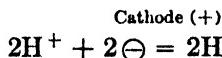
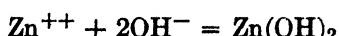
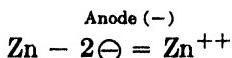
FIG. 16. Perforations in anodes of an Edison primary cell. (a) shows the beginning of exhaustion, as indicated in the panels. (b) shows that the element is almost exhausted, and (c) shows that the element needs to be replaced. (*Courtesy Thomas A. Edison, Inc.*)

thickness according to the capacity of the battery. These panels are designed to perforate gradually so as to indicate the state of exhaustion. In later types, the panels are designed to provide progressive indications of exhaustion; this is done by having two or more panels of different thicknesses in each outside zinc electrode. The panels perforate successively, indicating different stages of exhaustion, as shown in Fig. 16.

The electrolyte consists of a sodium hydroxide solution, of 20 to 25 per cent concentration. The cell system is



Actually the CuO and Cu are unstable in the presence of caustic and form intermediate oxides. The electrode reactions and the secondary reactions may be represented as



The copper oxide acts as a depolarizer by removing the hydrogen practically as fast as it is formed. If the caustic solution is made with too high a concentration, the electrolyte, toward the end of the life of the cell, will not hold zinc hydrate in solution, and its crystallization will result, with the formation of octahedral transparent crystals. This is particularly noticeable at low temperatures.

The cell as made up may consist of a single element composed of two zinc anodes connected in parallel, and a copper oxide cathode suspended between them; or the electrodes may be assembled in multiple, consisting of two copper oxide and three zinc plates. The electrodes are assembled into an "element" which can be purchased for replacement purposes, as can also sodium hydroxide (caustic soda) put up in cans containing the right amount for a cell of any size. The cell container is usually made of glass but may be made of enameled iron instead. A layer of heavy mineral oil is poured over the electrolyte to prevent evaporation and to keep the caustic soda from "crawling" up the cell terminals or from absorbing carbon dioxide.

The open-circuit voltage varies from about 0.9 to 1 volt. By the addition of sulphur in amounts of 1 per cent or less, it has been found possible in the Columbia copper oxide cell to raise the operating voltage by approximately 0.1 volt. In this cell granular copper oxide is used, packed into an iron basket.

The Lalande cell is one of the most efficient and satisfactory batteries in use when applied to suitable classes of service. It is rugged, relatively cheap to make and operate, and reliable in its action, and it has a high current output per unit of volume. It requires no attention for long periods of time and has excellent continuous-discharge and heavy-duty characteristics. It can be made dry or non-spillable by adding a small quantity of starch, or by making a paste out of the electrolyte and magnesium oxide. It is used widely as the normal or stand-by power supply for railroad signal systems, warning signs, particularly the flashing-light type at railroad crossings, fire and burglar alarms, and electrically lighted aids to navigation. Over a million copper oxide cells are made in the United States annually, ranging in capacity from about 300 to 1000 amp-hr., and capable of delivering from 1 to 5 amp.

Eveready Air Cell. The Eveready Air Cell⁹ is a product of the National Carbon Company, and derives its name from the principle of air depolarization. It is shown in section in Fig. 17. The anode is made of heavily amalgamated zinc; the cathode of porous amorphous carbon. This may be a lampblack-charcoal composition processed to be capable of sorbing atmospheric oxygen and making it available in electrochem-

⁹ G. W. Heise and E. A. Schumacher, *Trans. Electrochem. Soc.*, **62**, 383 (1932).

ically active form. A wet cathode will not function in this manner; therefore it is given a special waterproofing treatment that makes it electrolyte-resistant without destroying its gas-absorptive properties. The electrolyte consists of a 20 per cent solution of sodium hydroxide so that the cell system is

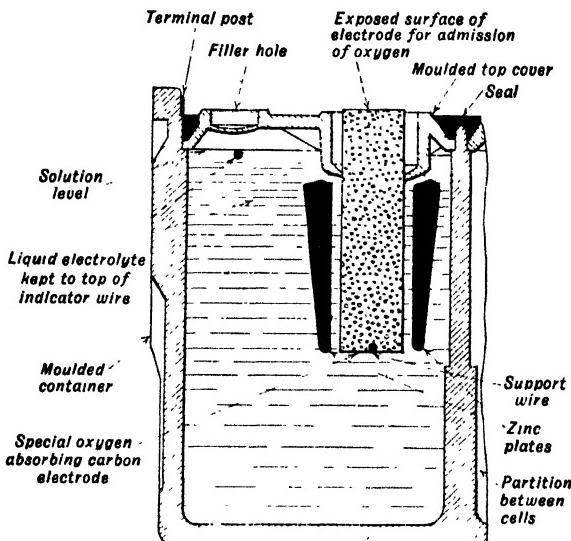
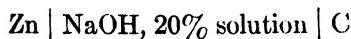
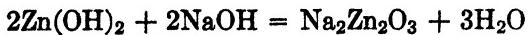
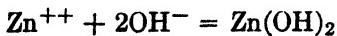
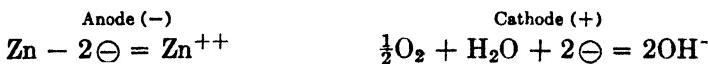


FIG. 17. Eveready Air Cell. (*Courtesy National Carbon Company.*)

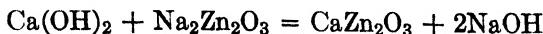
The open-circuit voltage of a fresh cell is 1.46 volts; the operating voltage for ordinary loads is 1.2 to 1.25 volts. The electrode reactions and the secondary reactions may be represented as:



The oxygen in the cathode reaction above is obtained from air absorbed to the porous carbon electrode.

The caustic soda in the form of the monohydrate, $\text{NaOH} \cdot \text{H}_2\text{O}$, which has a low melting point, is molded in solid dry form about the carbon and zinc electrodes at the time of manufacture. The addition of ordinary drinking water is all that is needed to prepare the battery for service. This particular cell contains solid hydrated lime which reacts

with the exhausted solution to precipitate zinc and regenerate the electrolyte, thus:



This results in greatly increased capacity per unit of volume, a commercial cell of 2,250 cc. of electrolyte being capable of delivering 750 amp-hr. The cell is normally capable of operating at 3.5 to 4.5 amp. per sq. ft. of cathode surface area without appreciable polarization; by using a hollow electrode¹⁰ so that the distance from air to active electrode surface is minimized, this rate can be at least doubled.

The air cell is available in different sizes, nominal ratings being 300 to 600 amp-hr., in single and multiple-cell units. Its principal uses are in radio A, telephone, and railway track circuits, and because of its flat discharge curve it has found extensive application in potentiometer and allied uses in which well-sustained voltages are desirable.

Fery Cell. The Fery cell, now seldom found in America, but used in France, also employs oxygen from the air as a depolarizer in a porous carbon electrode. The system of the Fery cell is $\text{Zn} | \text{NH}_4\text{Cl} | \text{C}$, and it has an open-circuit e.m.f. of about 1.2 volts. The mechanical construction differs considerably from that of the Eveready cell illustrated.

Fuel Cells. Of no practical importance up to the present, but of theoretical interest, is a primary cell in which a carbon and an oxygen electrode dip into a suitable electrolyte so that a current will be produced when the external circuit is closed. In this way electrical energy would be obtained by the union of carbon and oxygen without the intermediate step of the production of heat. Quite a number of investigators have attempted the production of such a cell; these attempts are ably summarized by Thompson,¹¹ Allmand,¹² and Baur and Tobler.¹³ It can be calculated that the voltage of such a cell at room temperature would be 1.04 volts, and that 1 kilo of carbon would furnish about 8,940 amp-hr., or 10.2 kw-hr. On this basis it would require about 0.3 lb. of coal of the average type used for steam production to produce 1 kw-hr., as against 1.37 lb. which represents the average practice for public utilities.

If such a cell were obtained, it is easy to imagine the rapid extension of electrical energy, the supremacy of coal over water power, the abatement of the smoke nuisance, and the vast changes in engineering and chemical industries.

¹⁰ G. W. Heise, *Trans. Electrochem. Soc.*, **75**, 155 (1939).

¹¹ M. DeKay Thompson, *Theoretical and Applied Electrochemistry*, Macmillan Company, New York, 1939.

¹² A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, Edward Arnold and Company, London, 1924.

¹³ E. Baur and J. Tobler, *Z. Elektrochem.*, **39**, 169 (1933).

CHAPTER IV

SECONDARY CELLS OR STORAGE BATTERIES

Secondary or storage cells are voltaic cells that after discharge can be brought to their original state by passing a current through them in a direction opposite to that of the discharge current. The charging of storage cells may be considered to be a condition produced by polarization. In this connection it may be noted that the polarization observed by Gautherot in 1802 while decomposing water electrolytically led Ritter to repeat the experiment more extensively to study the possibility of storing electricity.

A storage battery is composed of two or more cells. However, since nearly all applications of storage cells require a number acting as batteries, the expression storage battery is used so commonly that it is frequently applied even though but one cell is involved.

The first practical storage battery was developed by Planté, who began his studies in 1859. He rolled two sheets of lead, separated by strips of rubber, into the form of a spiral, and immersed this element in a 10 per cent solution of sulphuric acid. He found that by repeatedly charging and discharging the cell the capacity to "store" electricity could be increased. This is the basis at the present time of developing one type of storage-battery plates called formed plates.

A storage cell does not store electrical energy, although Ritter considered the polarization he obtained as storage of electrical energy somewhat as a condenser stores electricity. A storage cell converts electrical energy into chemical energy and then is capable of reconverting this chemical energy into electrical energy.

In the more than three-quarters of a century during which storage cells have been developing, only two or three commercially successful types have been produced. One is the common lead-acid cell; another is the nickel-iron-caustic or alkaline cell, developed by Edison. We may therefore, for the sake of brevity, classify storage cells as acid cells and alkaline cells.

Storage cells may be considered electrolysis cells during the charging process and voltaic cells during the discharging process. The same nomenclature as regards positive and negative electrodes, anode and

cathode, and direction of current has been adopted as for electrolysis cells. Figure 18 illustrates the terminology used in connection with acid and with alkaline storage cells.

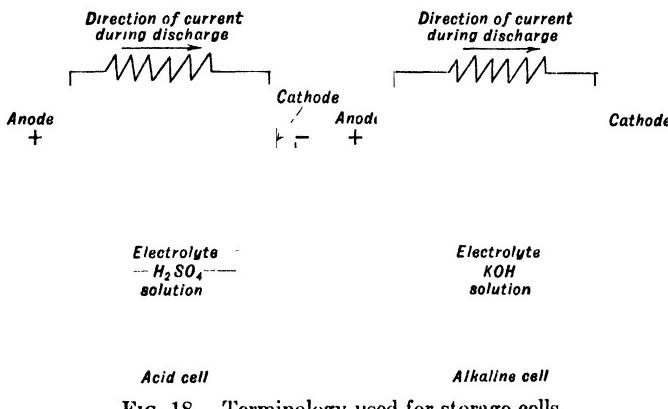
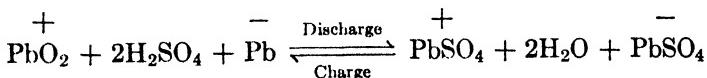


Fig. 18. Terminology used for storage cells.

ACID STORAGE CELLS

The acid storage cell in the charged condition consists of the system $\text{PbO}_2 \mid \text{H}_2\text{SO}_4 \mid \text{Pb}$. On discharge of the cell the lead peroxide and the lead are both converted to lead sulphate. The reactions during charge and discharge may be represented by the following equation, as regards the final products:



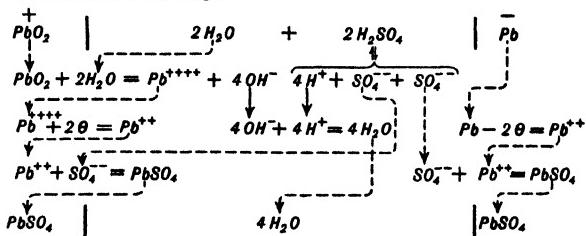
Theoretically it is immaterial which electrode is called positive and which negative in a completely discharged battery, but practically the polarity must not be reversed, for in a normally discharged battery a good deal of the lead peroxide and lead is not converted to the sulphate.

A number of theories have been proposed to account for the processes taking place in a storage cell during charge and discharge. The reaction given above is that of the double-sulphate theory, which is the one most commonly accepted at present. The expression "double-sulphate" refers to the formation of lead sulphate at each electrode during discharge. The most important fact to support this theory is that it is capable of thermodynamic proof.¹ The equations in Fig. 19 give a more

¹ G. W. Vinal, *Storage Batteries*, third edition, p. 165, John Wiley & Sons, New York, 1940. The author cites further evidence to support this theory, and also discusses a number of other theories that have been proposed.

SECONDARY CELLS OR STORAGE BATTERIES

Reactions during discharge:



Reactions during charge:

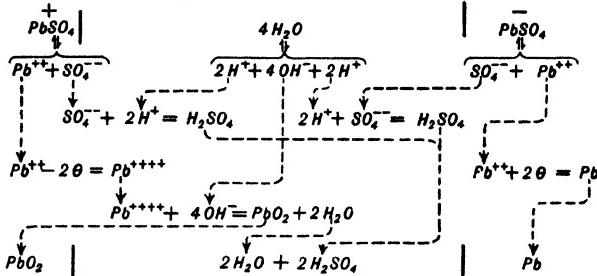


FIG. 19. Reactions taking place in a lead storage cell.



FIG. 20. An installation of 60 storage cells with a capacity of 120 ampere-hours at the 8-hour rate. (Courtesy The Electric Storage Battery Company.)

complete picture of the probable reactions taking place in a cell during the processes of charge and discharge.

Materials for Cell Construction. The containing vessels for the smaller and medium-size stationary units are made of glass as shown in Fig. 20. For large stationary units the container is made of wood, lined with lead; for portable batteries hard rubber is used quite commonly.

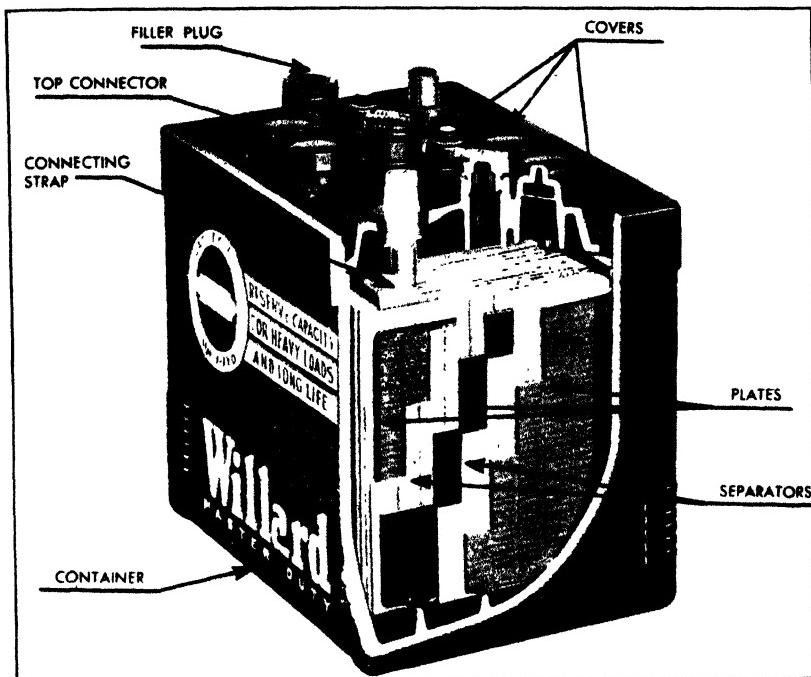


FIG. 21. Storage battery, portable type.

The positive and negative electrodes called plates are assembled alternately; all positive plates are connected in parallel to a connecting strap, and all negative plates are likewise connected to another strap. The plates are hung from the cover or supported on the bottom of the container, and the plates are kept apart by suitable insulators called separators. In practically all cells the end plates are negative, so that a cell usually has one more negative plate than it has positive plates. The electrolyte consisting of a sulphuric acid solution is of such amount that all the plates are completely immersed. The construction of a portable battery is shown in Fig. 21.

A portable radio battery with a transparent plastic case and spill-proof cover is shown in Fig. 22. The battery may be tilted in any position

without loss of electrolyte. It is constructed with a built-in indicator: a green ball sinks when the battery is 10 per cent discharged; a white ball, when it is 50 per cent discharged; and a red ball, when it is completely discharged. As the battery is recharged the balls float again.

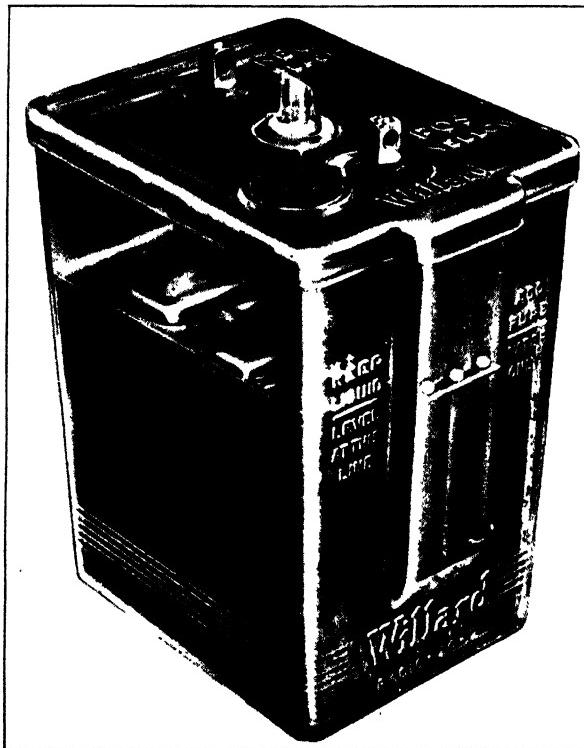


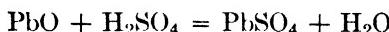
FIG. 22. Radio battery, with plastic case and cover.

Types of Plates. Two general methods are in use for construction of the plates. In one type, called Planté plates, or formed plates, the active material is formed electrochemically on the surface of lead plates. In another type, grids are made from antimonial lead and the active material is supported by the grids which are made in lattice form. Such plates are sometimes called Faure plates but more commonly pasted plates.

Pasted Plates. In pasted plates a grid is formed of antimonial lead. The grid serves two main purposes: it acts as a support for the active material, which has little mechanical strength of its own; and it provides a fairly uniform current distribution throughout the plate, especially for the positive plate, for the electrical conductivity of the grid material is many thousand times that of lead peroxide.

The grid contains 5 to 12 per cent antimony. The antimony aids in the casting of the grid, and on solidifying causes a slight expansion so that sharp castings are produced. The antimony also adds mechanical strength to the grid and serves to resist electrochemical corrosion of the grid, but it increases the electrical resistance.

The active material is derived from the electrochemical reaction on a paste composed of one or more of the oxides of lead and a liquid. The liquid may be a sulphuric acid, magnesium sulphate, or ammonium sulphate solution, or it may be only water. If water is used alone the pasted plate is later dipped into a sulphuric acid solution. The paste is worked into the grid by manual labor or by special machines. The oxides of lead used for the paste are chiefly litharge, PbO , and red lead, Pb_3O_4 . These oxides may be used singly or in combination with each other. The sulphuric acid reacts with the lead oxides to form lead sulphate, which has a cementing action and therefore holds the active mass together. The reactions may be represented as



and



In order that the finished active material may possess desirable physical properties several accessory materials may be added to the paste.² Magnesium sulphate, sugar, or barium saccharinate, called porosity agents, may be added; they dissolve out of the plates when the setting process has been completed. Hardeners and binders are added to increase the strength of the finished plate. Glycerin, because it reacts with litharge to make a cement, is commonly used for this purpose. Another class of materials called expanders is frequently added to the paste for the negative plates. The sponge lead changes size with charge and discharge, and during the life of the plates there is a tendency toward a general shrinking and compacting so that the plate may become practically useless. Inert materials are therefore added to reduce this contraction and compacting. Barium sulphate, graphite, and wood flour are some of the materials used for this purpose.

The pasted plates are allowed to dry, which may require from a day to several days. They are then hung in a sulphuric acid solution ranging in specific gravity from 1.100 to 1.200 and are electrolyzed for a period of a day or more. The plates which are to become the positives are made the anodes in the forming tank, and the plates for negatives are made the cathodes. The anodes are oxidized to lead peroxide, and the cathodes are reduced to lead.

² G. W. Vinal, *Storage Batteries*, third edition, John Wiley & Sons, New York, 1940.

In the box-negative plates manufactured by The Electric Storage Battery Company, the lead oxide paste is placed in compartments in lead-antimony grids and are held in place by a covering of perforated lead sheet. A box-negative is shown in Fig. 23. In the iron-clad positive, put out by the same company, a slotted hard-rubber tube is filled with the lead oxide paste. The tube contains a central lead rod serving as a conductor. A number of such tubes are mounted vertically in a grid to form a plate as shown in Fig. 24.

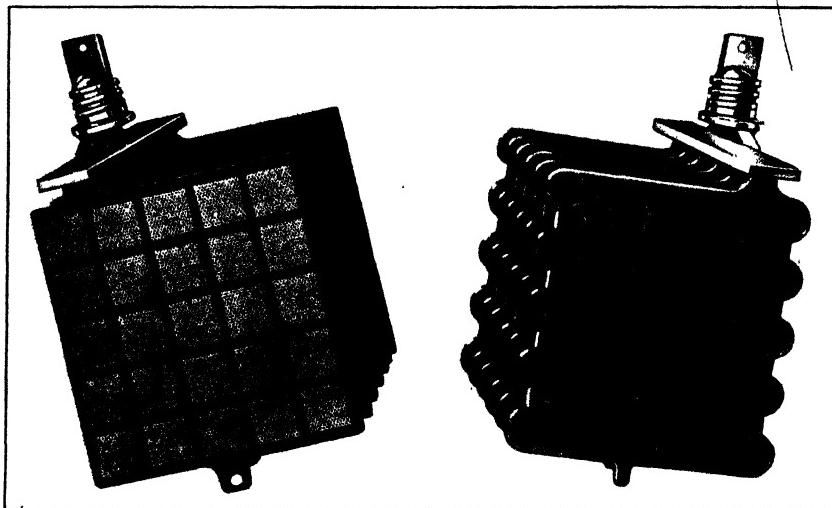


FIG. 23. Box-negative (left) and Manchester positive (right) plate. (*Courtesy The Electric Storage Battery Company.*)

Planté Plates. In Planté or formed plates the active materials, sponge lead and lead peroxide, are derived electrochemically from the lead of the body of the plate. Planté plates are heavier and larger than pasted plates for equal capacity. They are therefore used for stationary batteries where bulk and weight are not so important as durability. They are also used to a limited extent for train lighting.

In order to increase the amount of active material that can be formed, the surface of the blank lead plate is increased mechanically. This can be done in several different ways. In the spinning process the lead blank is passed back and forth between revolving mandrels which hold a large number of steel discs properly spaced. In the swaging process a swaging block with the plate design cut in its surface is rocked back and forth under pressure over the lead blank, thus pressing the lead into the desired form. In the so-called plowing process a tool is made to pass through the lead in such a manner that a furrow is cut and a leaf is

thrown up on one side of the furrow. By moving the plate the proper distance and repeating the plowing process, another leaf is produced, and so on. In another type of positive plate called the Manchester positive,

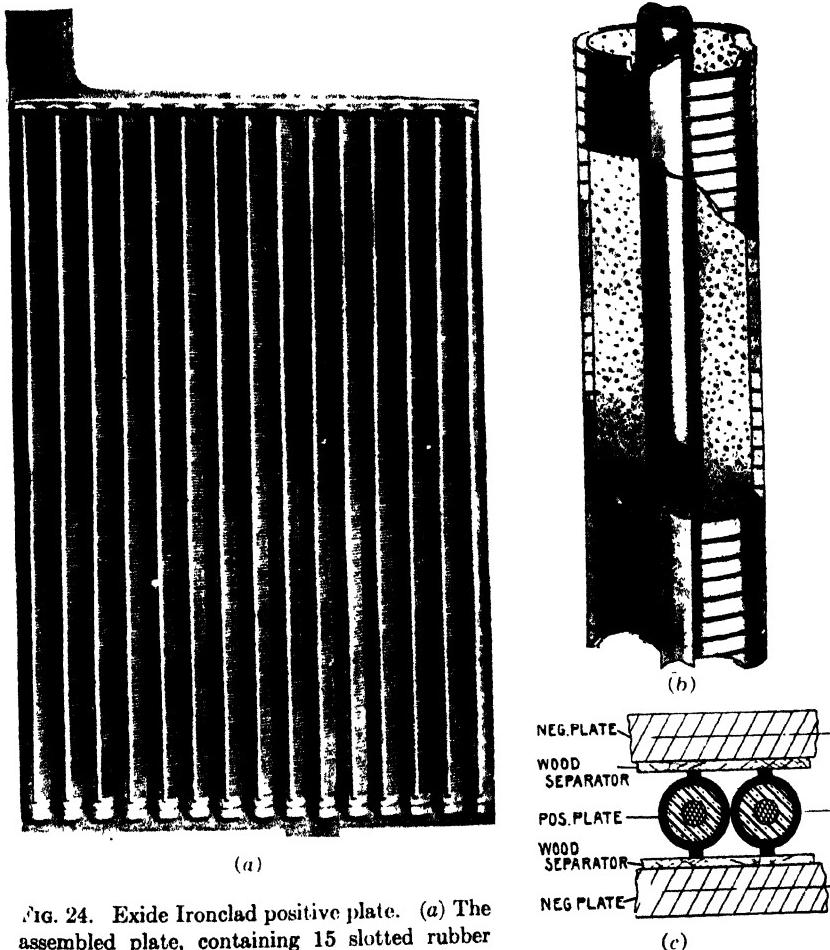


FIG. 24. Exide Ironclad positive plate. (a) The assembled plate, containing 15 slotted rubber tubes. (b) Longitudinal section of a slotted rubber tube. (c) Cross-section of a portion of a positive plate with a separator and a negative plate on either side. (Courtesy The Electric Storage Battery Company.)

a heavy grid of antimonial lead is cast with a large number of round holes. Ribbons of crimped lead are then rolled into the form of buttons or "rosettes" as shown in Fig. 25, and these are forced into the holes in the grid. This type of construction is shown in Fig. 23. In Europe a method of casting the plates directly with a highly developed surface has proved practicable.

The lead plates with their increased surface area are placed in a forming bath which consists of a sulphuric acid solution of about 1.1 sp. gr. If two lead plates are placed in a sulphuric acid solution there will be formation of lead sulphate wherever lead is not protected by an oxide film. On electrolysis, the sulphate and oxide on the anode will be converted to lead peroxide, PbO_2 , while that on the cathode will be changed to sponge lead. If the current is then cut off, lead peroxide on the anode and the underlying lead will form a local couple, and the peroxide and

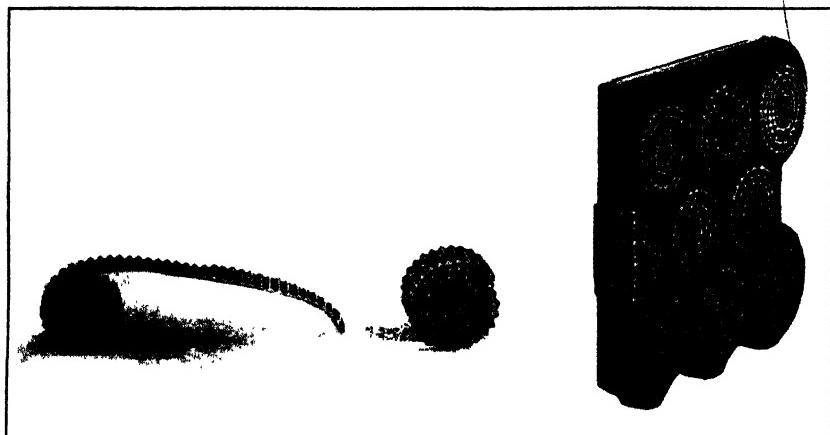


FIG. 25. Rosettes for Manchester positive plates. (*Courtesy The Electric Storage Battery Company.*)

an equivalent amount of lead will be converted to lead sulphate, but at the sponge lead cathode no change will occur. On further electrolysis all the lead sulphate on the anode will be converted to lead peroxide. By repeating this process the positive plate is formed, although the amount of lead converted into active material decreases progressively with repeated cycles of charge and discharge. This method of forming plates requires from 30 to 40 days, but the process can be hastened by the addition of "forming" agents to the forming bath. The forming agent is generally an acid that will form soluble lead salts. These salts are immediately precipitated as lead sulphate by the sulphuric acid with regeneration of the forming agent. The lead sulphate is then converted electrochemically to lead peroxide. Nitric acid and acetic acid are commonly used as such agents; other possible agents are chlorates, perchlorates, fluorides, chlorides, bichromates, permanganates, formic acid, and alcohol. After the forming process the plates are carefully washed to remove all forming agents. The forming process as described produces positive plates only. Negatives of sponge lead are produced by making

some of the positives the cathodes and electrolyzing them until the lead peroxide is converted to sponge lead.

Separators. In order to permit compact construction of storage cells, separators are placed between the alternating positive and negative plates in order to prevent short-circuiting by direct contact. Even if the plates are not in very close proximity, subsequent buckling of the plates or the formation of "trees" on the negative plates may cause direct metallic connection from one plate to another.

Separators are made from non-conducting porous materials; wood is very commonly used for their construction. Douglas fir, cedar, cypress, redwood, basswood, poplar, and some kinds of pine are suitable. The wood separators are made in the form of thin sheets with ribs on one side. In the assembly of the cell the separators are placed with the ribs running vertically and next to the positive plates. Wood separators gradually deteriorate in contact with the acid; the lead peroxide which is a strong oxidizing agent also attacks the wood.

Perforated rubber separators are used in some cases in conjunction with wood separators. They are made of thin sheets of perforated or slotted hard rubber and are placed next to the positive plates.

The threaded rubber separators used by the Willard Storage Battery Company are cut from a block of vulcanized rubber stock into which have been incorporated innumerable cotton threads running parallel to each other. The block is cut into sheets at right angles to the threads. The cut sections are pressed into a corrugated form and are stiffened with ribs. A separator for a starting and lighting battery has nearly 200,000 threads to the separator. Part of a threaded rubber separator is shown in Fig. 26.

The Gould Storage Battery Company has developed a separator made of matted glass fibers held together with a special paste which is not attacked by the acid electrolyte. These separators are used in connection with wooden ones.

A special separator called "Mipor" is manufactured by The Electric Storage Battery Company. It is made of vulcanized sponge rubber and is permeated with innumerable microscopic pores, so small that there are said to be approximately three billion pores per square inch of surface.



FIG. 26. Part of a threaded rubber separator. (Courtesy Willard Storage Battery Company.)

The Electrolyte. The electrolyte of the lead-acid storage cell consists of a sulphuric acid solution. The concentration of the acid is such that the specific gravity of the cell when charged ranges from about 1.200 to 1.300, depending upon the nature of the cell and the use to which it is put. There must be enough sulphuric acid in the cell to give the cell its full capacity, and in addition there must be enough extra to keep the

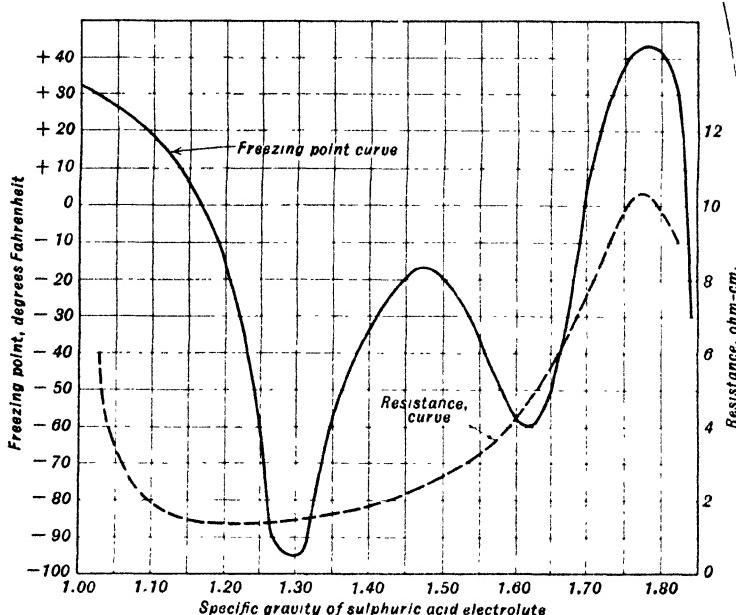


FIG. 27. Change of resistance and of freezing point with specific gravity of electrolyte of acid cells.

conductance sufficiently high when the cell is discharged. The effect of acid concentration on the resistivity of the acid solution is shown in the graph in Fig. 27. For compact cells, therefore, the concentration must be fairly high. There is an upper limit to the concentration of the acid. Local action, especially on the negative plate, increases rapidly with increasing concentration of the acid. This is particularly true in batteries used in warm locations as the tropics. Too high concentration of acid also destroys wooden separators. On the other hand, if sufficient active material is available on the plates the capacity of the battery is increased by higher concentrations. High concentration of the acid also increases the voltage of the battery as shown in Fig. 28 and lowers the freezing point of the battery as shown in Fig. 27.

The sulphuric acid and the water used for the electrolyte should be

pure. The water should preferably be distilled, but in some cases city water may be satisfactory.³

Attempts have been made to add absorbing materials to the electrolyte to prevent possible spillage. One of the most successful of these agents is sodium or potassium silicate. It forms a jellylike mass in contact with sulphuric acid. Other materials that have been used during the past 40 years are albumen, ground clay grog, starch, pumice, cellulose, plaster of Paris, asbestos, and fuller's earth. However, no absorbing materials have proved sufficiently practical to find extended use. Absorbing agents increase the internal resistance of the battery,

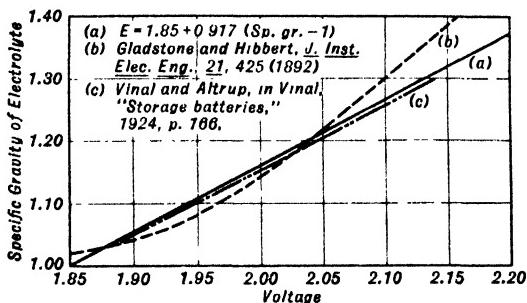


FIG. 28. Relation between voltage and specific gravity of electrolyte of acid storage cells.

decrease the capacity, and shorten its life. The Concordia Electric Company, Pittsburgh, Pennsylvania, manufactures an electric safety lamp, for use in mines, equipped with a storage cell with a solid electrolyte.

Cell Characteristics. Voltage. The voltage of acid storage cells is a function of the concentration of the acid in the electrolyte and also of the temperature. The open-circuit voltage of a cell in good condition can be approximated by the following formula

$$E = 1.85 + 0.917(G - 1)$$

where G is the specific gravity of the electrolyte. The relation between voltage and specific gravity of the electrolyte is indicated in the curve in Fig. 28. Figure 29 gives the relation between voltage and temperature, which shows that the voltage increases with increasing temperature. The temperature coefficient of the voltage is 0.000398 volt per degree C. (0.000221 volt per degree F.). The open-circuit voltage of the cell ranges between 2.00 and 2.14 volts for customary acid concentrations, but the

³ L. B. Crocker, M. Arendt, and R. F. Kuns, *Storage Batteries*, American Technical Society, Chicago, 1933.

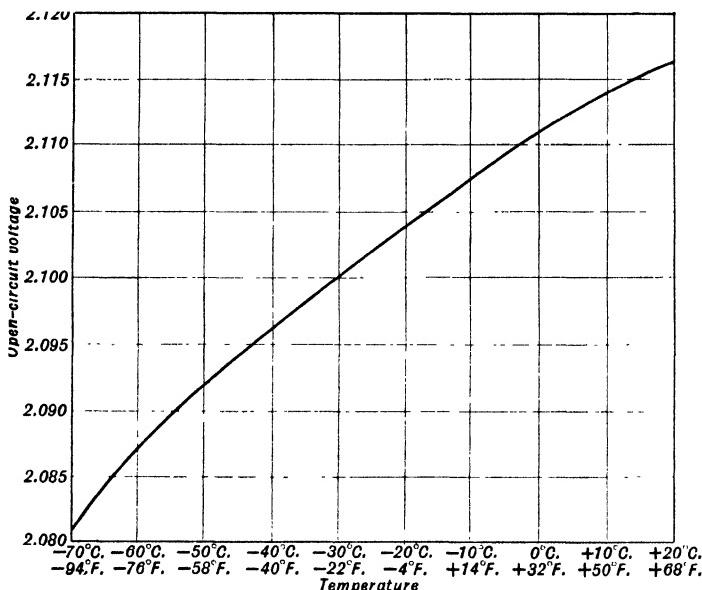


FIG. 29. Variation of voltage with temperature of acid storage cells. (Sp. gr. of electrolyte—1.280 at 25° C.)

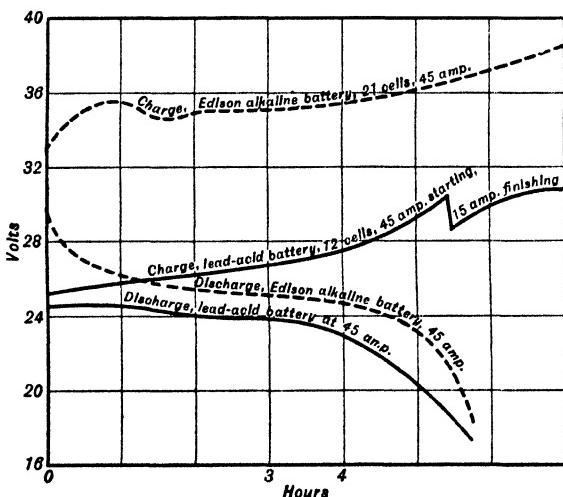


FIG. 30. Typical charge and discharge curves for Edison alkaline and lead-acid storage batteries. Each battery has an ampere-hour capacity at the 5-hr. rate of approximately 225. The charge curves show a constant current charge of 45 amp. for the Edison battery, and a step method for the lead battery with 45 amp. at the start and 15 amp. at the finishing stage.

nominal voltage of the acid storage cell is generally considered to be 2 volts. Typical charge and discharge curves for acid cells are shown in Fig. 30.

Capacity. The capacity of storage cells depends upon the amount and condition of active material (lead peroxide and sponge lead), the shape and arrangement of the active material, the concentration of the electrolyte, the temperature, and the discharge rate in amperes.

The amount of active material in a single plate is limited by several factors. On discharge of the battery, lead sulphate is formed; this

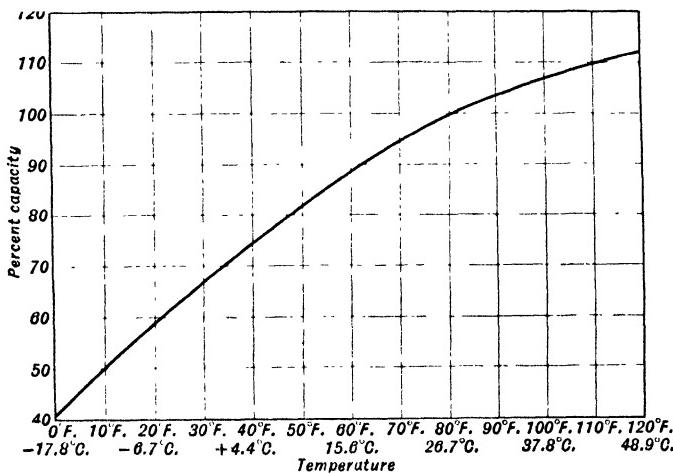


FIG. 31. Effect of temperature on the capacity of acid cells.

increases the resistance of the plate and also hinders diffusion of the acid toward the active material. It is impossible to utilize all the active material in the plates. The ratio of the active material taking part in the reactions to the total active material present in the plates has been called the coefficient of use. The average coefficient of use of good acid batteries is about 0.25. For a given amount of active material thin porous plates have a greater capacity than thick or dense plates.

The capacity of storage cells is affected very much by temperature as shown in the curve in Fig. 31. Assuming the ampere-hour capacity to be 100 per cent at 80° F. (27° C.), it is only 50 per cent at 10° F. (-12° C.).

The capacity of storage cells is sometimes expressed as the watt-hour capacity, but more commonly as the ampere-hour capacity. The ampere-hour capacity multiplied by the average discharge voltage is equal to the watt-hour capacity. For approximations the discharge voltage

can be taken as 2 volts per cell, although this varies according to the service to which the battery is subjected.

In testing a storage battery for its capacity, the result obtained will depend to a marked degree upon three factors: (1) the rate at which the battery is discharged, (2) the temperature, and (3) the voltage at which the test is terminated. When a battery is discharged, the acid in contact with the active material is consumed and the capacity of the battery will be dependent on the rate of diffusion of more acid to the active material. The voltage of the cell is not a function of the average specific gravity of the whole electrolyte, but only of the specific gravity of that part of the electrolyte in immediate contact with the active material. At a high discharge rate the final or cut-off voltage is attained more quickly than at a slow rate, in which diffusion can replace the acid more satisfactorily. The cut-off voltage is taken as the voltage at the end of the useful period for a particular service. For stationary batteries discharged at the 8-hr. rate this is 1.75 volts per cell.

The most common ampere-hour rating is the time rating by which the capacity is stated as the number of ampere-hours that can be delivered in a certain time. For stationary batteries the rating is 8 hr. or in some cases 6 hr.; for starting and lighting batteries it is 20 hr., and in some cases 20 minutes. The current to be used during the test is obtained by dividing the nominal ampere-hour rating by the number of hours for which the battery is rated. For short periods, batteries are rated in amperes for a certain length of time. For long periods, the ratings are in ampere-hours.

Efficiency. The efficiency of storage batteries may be expressed as ampere-hour efficiency and energy or watt-hour efficiency. The ampere-hour efficiency represents the ratio of the ampere-hours of electricity delivered by the battery to the ampere-hours required for a complete recharge. The energy efficiency represents the ratio of the watt-hours delivered by the battery to the watt-hours expended in charging it. The ampere-hour efficiency of lead-acid storage batteries is from 94 to 97 per cent; the energy efficiency ranges from 75 to 85 per cent. The difference in current and energy efficiencies is due to the difference in voltage between the charge and discharge, as shown in the curves in Fig. 30. This difference in voltage is due to the slowness of diffusion of the acid away from the active material during charge and toward it during discharge. This loss is therefore due to concentration polarization as explained in an earlier chapter.

Retention of Charge. An acid battery gradually loses its charge on standing idle, owing to the action of the acid on the plates with the formation of lead sulphate. At the positive plate the discharge is due

to electrochemical action between the lead peroxide and the lead of the grid, the sulphuric acid acting as the electrolyte of the local couple formed. The local action is more pronounced at the negative than at the positive plates. Certain impurities in the electrolyte hasten the discharge; among them, iron, copper, manganese, chlorides, nitrates, and acetates are especially harmful. Platinum is especially harmful in storage batteries, but is rarely found.

Self-discharge may also be the result of short circuits. These may be internal, caused by excessive sediment or defective separators, or external if the tops of the cells are wet with spilled electrolyte.

A good automobile battery should not lose over 30 per cent of its capacity during an idle period of four weeks; this corresponds to about 1 per cent a day.

Sources of Trouble. Various types of trouble, most of which are caused by abuse or improper care, may develop in lead-acid storage batteries. Some of the most common ones are as follows:⁴

Sulphation. Sulphation in storage batteries refers to the formation of abnormal lead sulphate, which cannot readily be converted to lead peroxide or sponge lead. It will be observed that the formation of lead sulphate is a normal result of discharge, and sulphation does not include this normal type because normal sulphate is readily converted. Sulphation is caused by allowing the battery to remain in a state of discharge or partial discharge for a relatively long period of time. The lead sulphate is but sparingly soluble in the electrolyte, and the finely divided sulphate will gradually go into solution and then precipitate on the coarser sulphate particles. There will then be formed a granular or coarse sulphate that can be converted only with difficulty. One remedy for sulphation is to pour out the electrolyte and refill the cells with water. After being allowed to stand idle for about an hour to permit more uniform distribution of the acid remaining in the pores of the plates, the battery is recharged until the specific gravity and voltage remain constant for 10 hr. The gravity of the electrolyte is then adjusted for the charged condition.

The level of the electrolyte may be below the tops of the plates. This will cause abnormal sulphation at the top, and eventually the plates may crumble. It may also cause overheating at high discharge rate, and it reduces the capacity of the battery.

Overcharging produces excessive gassing which loosens active material, especially at the positive plates. It may also cause an excessive rise in the temperature of the cells.

⁴ M. Arendt, *Storage Batteries*, D. Van Nostrand Company, New York, 1928; and G. W. Vinal, *Storage Batteries*, third edition, John Wiley & Sons, New York, 1940.

Undercharging of the battery, if continued, causes a gradual running down of the cell, and one or more of the cells may become exhausted or even reversed.

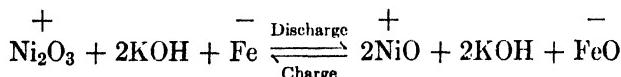
Buckling and warping of the plates may be caused by overdischarging and overcharging. Planté plates especially will gradually grow during repeated recharges, owing to continued forming of active material.

Shedding of the active material in the plates is more common in positive plates. The active material falls to the bottom of the jar, and the plates suffer a permanent loss in capacity. Shedding is caused by violent gassing toward the end of the charge. It can be reduced by careful regulation of the final charging current and by the use of close-fitting separators. Glass fiber separators have been used with considerable success; they fit close enough to hold the active material in place yet are porous enough to permit necessary diffusion of acid and migration of ions.

Freezing of the electrolyte is particularly observed in discharged or partially discharged batteries. By reference to the freezing curve, Fig. 27, it will be observed that a battery fully charged with a specific gravity of 1.280 has a freezing point of about -70° C. (-95° F.), whereas in a battery discharged to a specific gravity of 1.100 the freezing point is about -8° C. ($+18^{\circ}$ F.).

NICKEL-IRON ALKALINE STORAGE CELLS

Although there are a large number of acid cells on the market, the Edison is the only alkaline cell manufactured in the United States. Edison nickel-iron alkaline storage cells consist of the system: $\text{Ni}_2\text{O}_3 \mid \text{KOH} \mid \text{Fe}$. The electrolyte consists of a solution of about 21 per cent potassium hydroxide. The equation representing the charge and discharge of Edison storage cells may be considered to be as follows:



The equation may not be a true representation of the actual chemical changes taking place during charge and discharge. Quite a variety of equations have been proposed; and, since the electrolyte does not change appreciably in composition or concentration during charge and discharge, the difference in the equations proposed lies largely in the nature of the oxide of nickel when charged and when discharged, and the nature of the iron oxide when discharged. The oxide compositions that have

been proposed for the charged state are: NiO_2 , Ni_2O_3 , $\text{Ni}(\text{OH})_3$; for the discharged state: NiO , Ni_2O_3 , Ni_3O_4 , $\text{Ni}(\text{OH})_2$, and FeO , Fe_3O_4 , $\text{Fe}(\text{OH})_3$. It seems very likely that the oxides are hydrated. The equation given above is probably as closely true to the actual reactions, in the light of our present knowledge, as any that have been proposed. On the basis of this equation the actual reactions taking place within the cell may be represented as shown in Fig. 32.

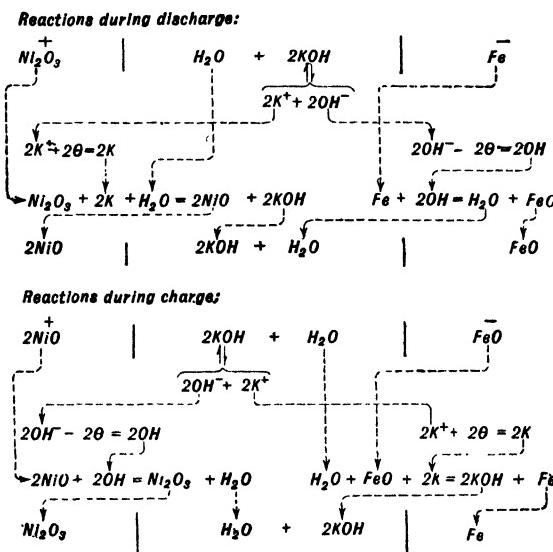


FIG. 32. Reactions taking place in an alkaline storage cell.

Positive Plates. In the positive plates the active material is contained in cylindrical perforated nickel-plated steel tubes; the tubes are assembled into a nickel-plated steel frame to form the plate, as shown in Fig. 33. The positive active material may be prepared by dissolving nickel shot in sulphuric acid. The hydrogen evolved may then be collected and used in the annealing of the nickel-plated grids and containers to produce a non-oxidizing atmosphere; the hydrogen may also be used in the reduction of ferric oxide to ferrous oxide. The purified nickel sulphate is sprayed into a hot sodium hydroxide solution. The nickelous hydroxide formed as a precipitate is collected, dried, and then leached with hot water to remove soluble impurities. After again drying, the hydroxide is ground and screened to 30 to 190 mesh.

To improve conductivity, nickel flake is added to the nickelous hydroxide in the Edison cell. The nickel flake is prepared by electrodeposition of alternate layers of nickel and copper on revolving cylinders. The cylinders, 10 in a group, are alternated 125 times from the copper

to the nickel tanks with a water rinse between each tank, a process requiring a total of about 5 hr. The copper-nickel sheets are stripped from the cylinders and are cut into squares $\frac{1}{16}$ in. on an edge. The copper is dissolved chemically, leaving 125 nickel flakes from each square.

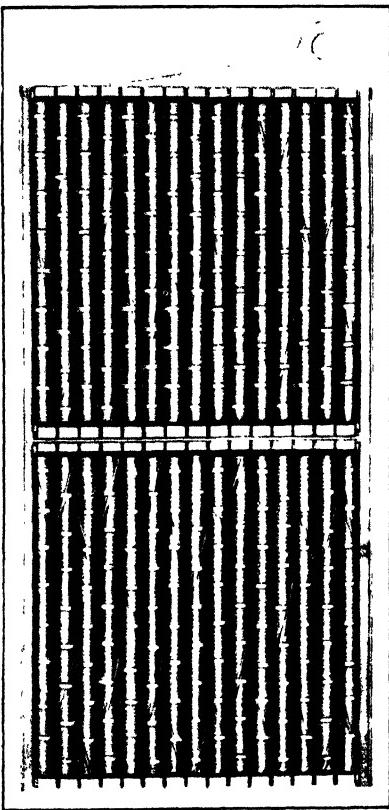


FIG. 33. Positive plate, Edison alkaline cell. (*Courtesy Edison Storage Battery Company.*)

The nickel squares are washed and dried; they are extremely light for their gross bulk when thus prepared, a bushel weighing but $4\frac{1}{2}$ lb.

The positive active material and the nickel flakes are tamped under a pressure of 2,000 lb. per sq. in. into perforated steel tubes made of cold-

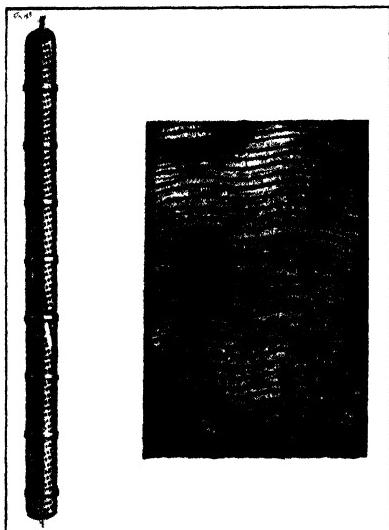


FIG. 34. Magnified longitudinal section of a positive tube, Edison alkaline cell. Light layers are nickel hydrate, dark layers are nickel flake. (*Courtesy Edison Storage Battery Company.*)

rolled carbon-steel ribbon which has 560 perforations per square inch. The ribbon is nickel plated and annealed to weld the nickel plate to the steel. The annealing is done in an atmosphere of hydrogen to prevent oxidation. The ribbon is wound spirally to form tubes $\frac{1}{4}$ or $\frac{3}{16}$ in. in diameter and $4\frac{1}{2}$ in. long. The seams are lapped and swaged flat.

The tubes are filled with alternate layers of the nickelous hydroxide and nickel flake, 315 layers of each to a tube. Figure 34 shows a magni-

fied longitudinal section of such a tube. For additional strength each tube is reinforced by 8 seamless nickel-plated steel rings. After the tubes are filled, the ends are pinched shut and are then clamped into permanent position in the nickel-plated annealed-steel grids, under mechanical pressure, forming the finished plate as shown in Fig. 33.

The Negative Plates. The active material of the negative plates is iron oxide. It is prepared in a finely divided form by dissolving pure iron in sulphuric acid. The gas liberated is collected and used the same as that liberated in the solution of the nickel for the positive plates. The ferrous sulphate, FeSO_4 , formed is recrystallized several times, then dried and roasted in an oxidizing atmosphere, forming Fe_2O_3 . The iron oxide is leached to remove traces of sulphate and is then dried and reduced in an atmosphere of hydrogen to iron, which is cooled in hydrogen and later oxidized to $\text{FeO} + \text{Fe}$. When ready to be used it is dried, ground, and mixed with 3 per cent of mercuric oxide. The mercuric oxide is reduced to mercury in the forming process and thus increases the conductivity and also helps to prevent the formation of ferric oxide.

The black iron oxide, FeO , and the HgO mixture is tamped into perforated nickel-plated steel pockets which are pressed into permanent position in a nickel-plated steel grid under hydraulic pressure, thus forming the negative plate as shown in Fig. 35.

In the charging of the new cells the nickel hydroxide of the positive plates is changed to nickel oxide, and the iron oxide is reduced to metallic iron.

The Electrolyte. The electrolyte consists of a 21 per cent solution of potassium hydroxide, KOH , with 50 g. of lithium hydroxide, LiOH , per liter of solution. The lithium hydroxide has a beneficial effect on

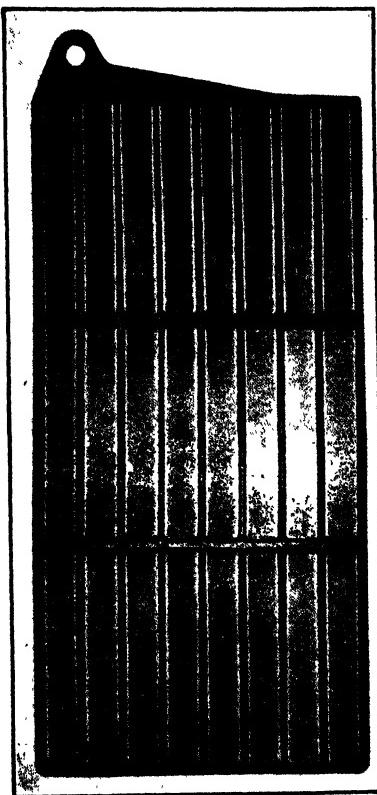


FIG. 35. Negative plate, Edison alkaline cell. (Courtesy Edison Storage Battery Company.)

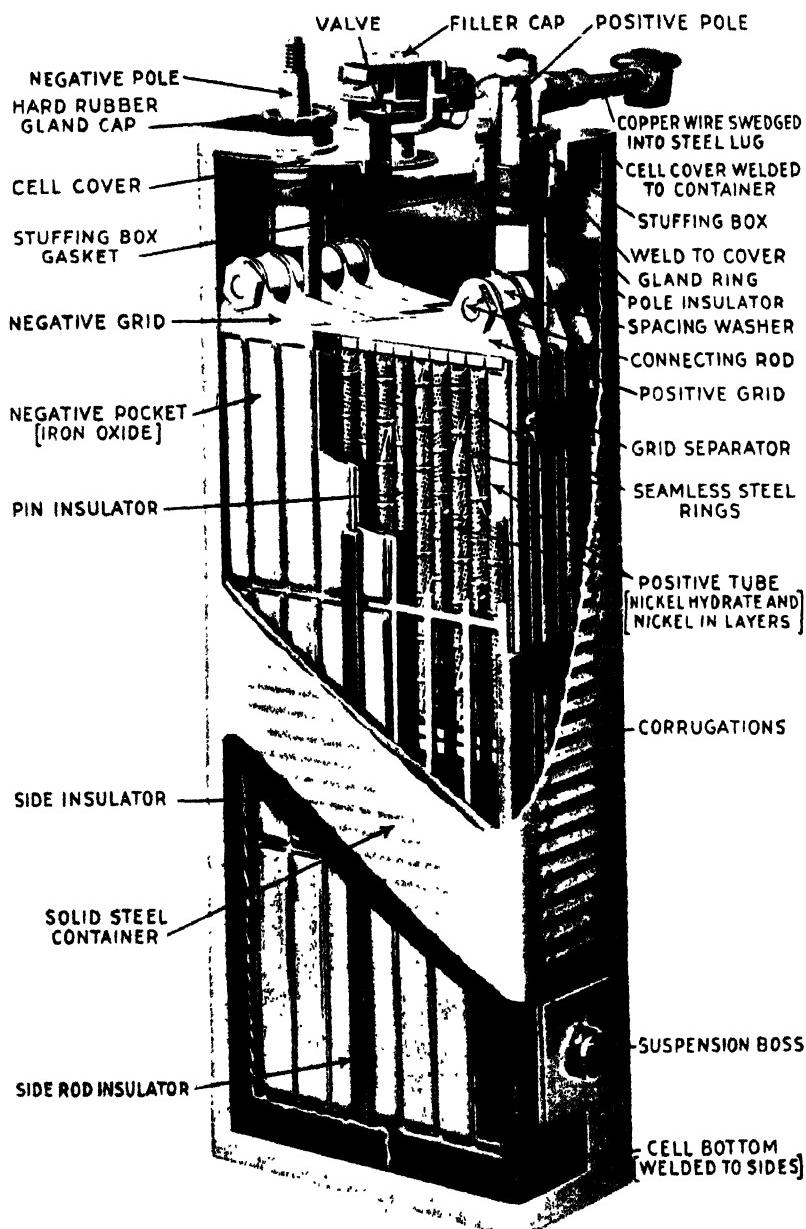


FIG. 36. An Edison alkaline storage cell. (*Courtesy Edison Storage Battery Company.*)

the voltage, capacity, and life of the cell, and its use is based entirely on the results of experiment.

The concentration of the electrolyte does not change appreciably during the discharge or charge of the cell. The gravity of the electrolyte, however, does gradually decrease in the course of normal service, and when it reaches the low limit of 1.160 at 60° F. with the solution at the proper level above plate tops the electrolyte should be replaced. The electrolyte of a cell may require renewal from one to three times during the normal life of the cell, depending upon the service to which the battery is applied and the care which it receives.

Assembly of the Cells. The proper number of positive plates are mounted on a steel connecting rod passing through suitable eyes at the top of each plate. The number of plates required depends upon the size of the cell. The plates are properly spaced on the rod by steel washers and are all locked together by means of a nut on each end of the rod. The negative plates are assembled in a similar manner, there being always one more negative than positive plate. The resulting positive and negative plate groups are interleaved as in the acid storage cells, but the conventional separators used in the latter are omitted; instead, the plates are separated by hard-rubber pins. Grid separators of hard rubber are used to keep the outside edges of the plates from making contact with the container, which is of nickel-plated steel. The terminal posts of the plate groups pass through openings in the top of the cell. A combined valve and filler opening at the top provides for proper escape of gases during charge, reduces evaporation, and prevents the carbon dioxide of the air from reaching the hydroxide solution in the cell. The cover of the filler opening is hinged to facilitate the periodic addition of water to the cells. An Edison alkaline cell is shown in Fig. 36.

Characteristics of Edison Cells. *Voltage.* The general shape of the charge and discharge curves of Edison alkaline storage cells, Fig. 30, page 78, are similar to those of acid storage cells, but the individual cell voltage is lower. The initial, average, and final voltages of Edison cells when discharging at their normal rates are about 1.5, 1.2, and 1.10 volts, respectively. At ampere rates which are lower and higher than normal these voltages are higher and lower respectively than those obtaining at normal rates.

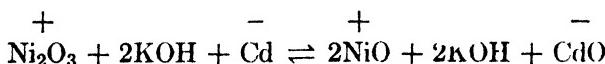
Capacity. The ampere-hour capacity of alkaline cells does not vary appreciably at widely different rates of discharge. Edison cells with lithium hydroxide in the electrolyte will increase in capacity for about 125 cycles of charge and discharge. The ampere-hour efficiency is about 82 per cent, and the watt-hour efficiency is about 60 per cent, both at the 5-hr. rate. The capacity of alkaline cells decreases with a

reduction in temperature. It acts similarly to an acid storage cell in this respect down to about 40° F., but below this temperature the capacity falls off more rapidly. After a full charge an Edison cell will lose 8 per cent of its charge during the first day of idleness, after which it loses about $\frac{1}{2}$ per cent per day. Edison cells may be left standing idle in a discharged condition indefinitely without injury. High rates of charge or discharge and overcharging of the cells also cause little or no injury.

NICKEL-CADMIUM ALKALINE STORAGE CELLS

Nickel-cadmium alkaline storage cells have found little application in this country but have enjoyed wide industrial use in Europe since 1930. The nickel-cadmium cell differs from the nickel-iron cell in the use of cadmium in place of iron for the negative electrode. The chief advantages credited to cadmium over iron are:⁵ (1) cadmium does not cause self-discharge to the same extent as iron; (2) it does not become passive at high rates of discharge at low temperatures; and (3) it requires a lower charging potential.

The active anode material, nickel oxide, is used exactly as in the nickel-iron cell, and the individual tubes and assembled plates look essentially the same as shown in Figs. 33 and 34. The electrolyte is a caustic potash solution with a specific gravity of 1.19 to 1.25, to which in some cells is added a little lithium hydroxide. The cell system is $\text{Ni}_2\text{O}_3 \mid \text{KOH} \mid \text{Cd}$. The main reactions involved in the charge and discharge of the cells can be represented by



The average discharge voltage is about 1.2 volts.

There are many applications of the battery in Europe, among which may be mentioned flashlights, signal and mine lamps, radio-set batteries and all types of military and emergency batteries; for traction purposes in tractors, automobiles, electric locomotives, and mine locomotives. The batteries are used for train lighting in all European countries, especially where trained servicing personnel is not available. They are giving excellent service in India, where trains in the mountains are subjected to extreme cold and in the valleys to extreme heat. The nickel-cadmium batteries, like the Edison batteries, are not injured by overcharging, deep discharge, or occasional short circuit.

⁵ Anna P. Hauel, *Trans. Electrochem. Soc.*, **76**, 435 (1939).

METHOD OF CHARGING STORAGE BATTERIES

Storage batteries may be charged by several different methods, depending upon the type of battery, the equipment available, and the type of service to which the batteries are subjected.

Constant Current. As its name implies, in the constant-current system, batteries are charged at a uniform current rate throughout the entire charging period. Edison alkaline cells may be charged by this method at rates up to and including the normal rate. When acid batteries are charged by this method the current is kept uniform until the batteries are charged to about 90 per cent of their ampere-hour capacity, after which the current is reduced to about 40 per cent of the initial value. The temperature of acid batteries should not exceed 110° F. (43° C.), although alkaline batteries receive little injury up to 115° F. (46° C.).

Rheostats must be placed in series with the batteries in order to keep the current constant as the voltage of the battery rises during charge.

Constant Potential. In the constant-potential method, batteries are charged at a constant voltage throughout charge. The minimum voltage required is about 2.2 volts per cell for acid cells and about 1.7 volts per cell for alkaline cells. In the constant-potential method the battery receives a relatively heavy current at the start, which drops rapidly as the voltage of the battery rises; this method of charging is therefore also called the tapering-current method. If the terminal voltage is of the proper magnitude, there is little danger of excessive gassing or of overheating of the battery toward the end of the charge.

In order to reduce the current rate during the early part of the charge and to increase it towards the end of charge, a resistance may be connected in series with the battery. The method is then called the modified constant-potential method of charging; it finds extensive use commercially.

Equalizing Charge. Batteries of the acid type used for operating trucks or tractors should be given an equalizing charge periodically; for batteries in steady service, this should be about once a week. The batteries are charged as usual until the normal end, after which the current is reduced to about half the finishing rate until all cells gas uniformly and the specific gravity of the electrolyte and the voltage have remained uniform for $1\frac{1}{2}$ to 2 hr. Alkaline cells require no such treatment.

Boosting Charge. If the capacity of a battery is not sufficient for the interval between regular charges, which is generally once a day after working hours, the battery may be given a short charge at a high rate,

at some convenient time, as during the noon hour, provided that electrolyte temperatures are kept within proper limits.

Trickle Charge. In trickle charging, the batteries are given a charge at a very low rate for a long period of time or continuously throughout their service. Trickle charging is used for acid batteries that are stored

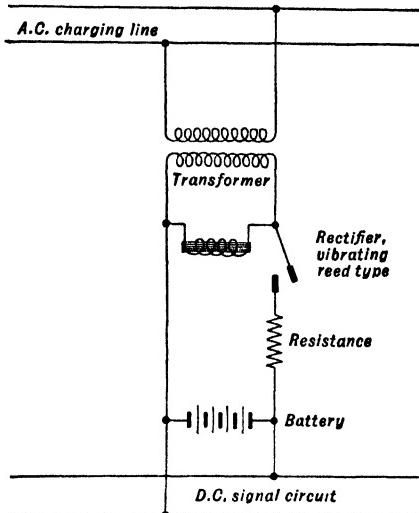
for relatively long periods. The current is then adjusted to just counteract local action within the cells so that the voltage and the specific gravity of the electrolyte remain constant. Stored alkaline cells require no such treatment. Trickle charging is also used for keeping batteries charged that are required to give intermittent service, as in radio and railway signal service. For this, the current is so adjusted that it will just restore that used in service and that lost by local action. Figure 37 shows the arrangement for trickle charging a battery for railway signal service. Trickle charging is used for acid and for alkaline batteries.

FIG. 37. Battery connected for trickle charging and for railway signal service.

Floating. A battery may be connected to a charging line so that its open-circuit voltage is slightly below the charging line voltage. The battery will then charge or discharge according as the voltage of the line rises or falls with power demands. Under these conditions the battery will automatically take care of the power requirements of a fluctuating load and will also be maintained in a charged condition. Batteries used for stand-by service may frequently be taken care of most satisfactorily by having them float on the power line. Although alkaline batteries may be floated, because of the wider spread between their charge and discharge voltage, they are not as well suited as acid batteries for this service.

APPLICATION OF STORAGE BATTERIES

Storage batteries are used in a large variety of applications, some of which are so well known that they are accepted as matter of fact. In many applications acid or alkaline batteries may be used; in others, one or the other type of battery is more suitable. In 1939 over 17 million



storage batteries were manufactured in the United States. Applications of storage batteries are so numerous that only a few leading ones can be mentioned here.

The greatest single application of storage batteries is for automobile starting and lighting, for which service nearly 16 million batteries were manufactured in the United States during 1929. They are also used for



FIG. 38. Industrial tractors propelled by storage batteries. (*Courtesy Edison Storage Battery Company.*)

starting aircraft, marine, and Diesel engines. Nickel-iron alkaline batteries in the type now manufactured in this country are not designed for low-voltage automobile starting service and are not used for this purpose.

Before the application of alternating current to radio, storage batteries filled an important field in radio reception, and they are still an important factor where alternating current is not available.

Storage batteries are widely used in trucks and tractors for handling baggage, freight, and materials at railway yards, warehouses, and factories. Storage batteries at one time found useful application in electric street trucks, especially for short-haul many-stop routes, as in department store, express, laundry, milk, bread, and ice delivery. The chief objection to electric trucks is their short radius of travel between

charges; it is for this reason that electric pleasure cars, quite popular during the first decade of the present century, are no longer in demand.

Battery-operated locomotives find application where city ordinances prohibit the use of steam locomotives, and where the more expensive construction of a third rail or overhead wire is not justified. Storage batteries are extensively used for the operation of mine locomotives, where they are in direct competition with overhead trolley and cable

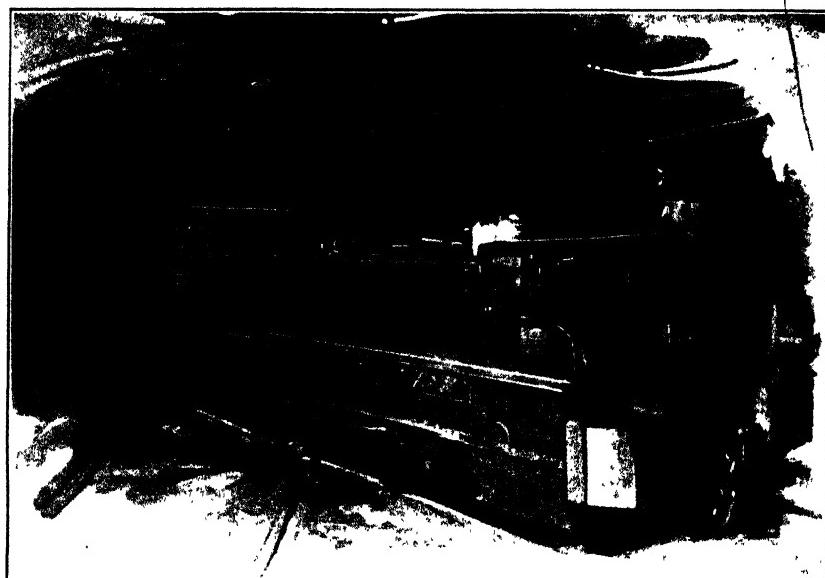


FIG. 39. A mine locomotive powered by a 48-cell storage battery. (*Courtesy The Electric Storage Battery Company.*)

reel locomotives. Sometimes the locomotives operate on power from a trolley wire on the main line but are switched to battery operation on spurs and during hours when the station power is shut off. Figure 39 shows a battery mine locomotive.

Submarine boats are operated entirely by storage batteries when submerged. The problem of avoiding spillage of the electrolyte and the formation of gas is an important one.

Storage batteries find important application in central electric stations. It is important that switchboard control, which is by means of relays and contractors, be independent of the main plant. Batteries are also used as stand-by service in the exciting of generator fields. Storage batteries may also be used especially in substations for stand-by service on the main line to maintain the voltage during peak loads, or to carry the load if the converters are put out of commission. However, owing

to the interconnection of power lines and the flexibility of modern steam plants for sudden loads, the need for storage batteries for the last purpose is much reduced. For downtown sections of large cities, storage batteries still play an important function in providing continuity of service. In the event of some disaster it is very important that street-railway, elevator, lighting, and telephone service be maintained. For stand-by service the batteries are often floated on the line; should the line voltage drop below a certain amount the batteries would help to carry the load automatically; at other times the batteries are being charged from the line. For trolley service, batteries may be located near a heavy load center or at the end of long feeders, thereby reducing copper costs.

Storage batteries also find application for isolated lighting plants, railway passenger-car lighting and air conditioning, and for multiple unit control and emergency lighting in electric trains.

A very important field for storage batteries is in railway signaling. In many cases for signal service the batteries are trickle-charged; they are connected to an alternating-current power line through a suitable rectifier and resistance and receive a very low charge continuously. An attempt is made to adjust the current in a trickle charge so that the charge received is equal to that used in service, plus that lost in the self-discharge of the battery. Figure 37, page 90, shows one scheme for connecting a battery to the signal circuit and for receiving a trickle charge.

In telephone service, storage batteries serve a variety of important purposes, for all the electrical energy used in connection with calls and for the operation of automatic mechanism is supplied by storage batteries.

Another important line of service for storage batteries is for emergency power and lighting other than central-station work. Many states require that, in all public buildings in which crowds gather, storage batteries be installed to take care of all lighting requirements for a certain period of time; the state of Pennsylvania, for instance, requires $1\frac{1}{2}$ hr. This includes schools, theaters, and hospitals. In the operating rooms of hospitals it is especially important that continued lighting be assured. In such services the batteries cut in automatically if the main power fails. Storage batteries are also used for stand-by service on board ship and in the operation of drawbridges, and they are desirable for stand-by service for passenger elevators. They are also used for assurance of continued power in some modern continuous sheet-glass plants where it is important that the sheet of glass be drawn without interruption. Storage batteries have also been proposed for power assurance in the tilting of Bessemer converters, for which compressed-air devices are

used at present to return the converters in the event of electric power failure. They are also used to insure continuous operation of gear hobbing machinery, where an interruption of the normal power supply might ruin expensive gears on which finished cuts are being made.

A relatively new application of storage batteries is for mine shuttle cars, which are essentially trucks designed for hauling coal on pneumatic tires under ground. These are now being used in large quantities in place of the conventional storage-battery locomotive.

Storage batteries find application to a considerable extent as a portable source of light and power, as in miners' electric cap lamps, for a source of constant potential in scientific work, and as a source of a large current at a low voltage.

CHAPTER V

ELECTROPLATING

In electroplating processes, metallic articles, and to a lesser extent non-metallic articles, are covered with a metal coating. A large proportion of electroplating has for its purpose the production of a decorative finish on a cheaper base metal. Sometimes, as in zinc plating, the object is the production of a corrosion-resistant surface; and frequently both purposes are accomplished at the same time. In some cases the plating produces a surface that resists mechanical wear, as in the chromium plating of dies and bearings. In still others, the electroplating serves to replace broken parts or worn surfaces.

Electroforming consists of the formation of articles by electrodeposition. The production of electrotypes is one large field of electroforming. In electroforming, the original surface on which the deposit is made is produced in the desired form out of suitable material, generally a non-metal, as, for instance, wax. The surface may be made conducting by the application of graphite or of a fine metallic powder. When the electrodeposition is completed the wax may be removed by melting, leaving the electroformed article.

PLATING EQUIPMENT

Current Generation. The direct current used in electroplating is of a comparatively low voltage. For most still plating other than chromium plating 6 volts is sufficient; for chromium plating and barrel plating 12 volts should be available. As the transmission of a low-voltage current is not practicable except for short distances, it is nearly always necessary to generate the direct current at the plating plant.

Most generators are coupled directly to the motor as illustrated in Fig. 40. For small plants requiring a small current the belt-driven motor-generator set may be most practicable. The generators are built in sizes ranging from 50 to 25,000 amp. at 6 or 12 volts. The large motor-generator set includes a 500-hp. motor, and the unit weighs well over 30 tons.

The winding of the generator may be series, shunt, or compound; from the point of constancy of voltage, the last type of winding is preferable.

It is generally considered unwise to install one generator of sufficient size to take care of all plating and cleaning requirements in the plant, although that would be the most economical in respect to original in-

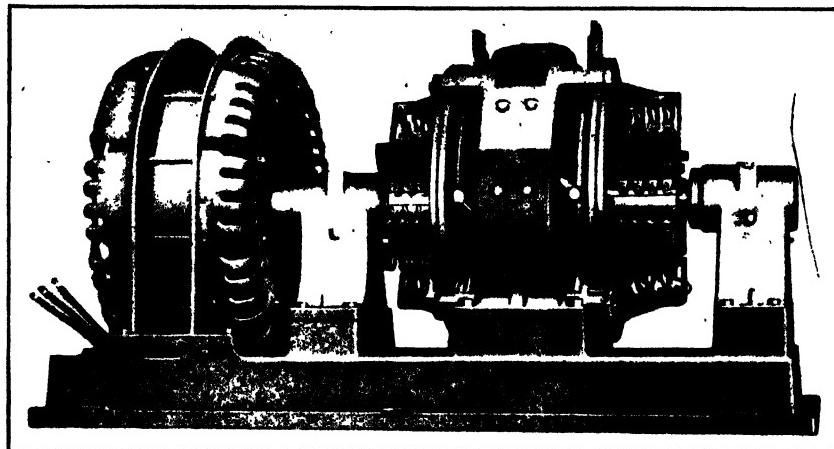


FIG. 40. Motor-generator set for electroplating. Generator, 2,000 amp., 6 volts; 20-hp. synchronous motor. (*Courtesy Chas. F. L'Hommedieu and Sons Company.*)

vestment. If continuity of operation is important, at least two generators are necessary to permit overhauling and repairs. If a variety of work is handled, a 6-volt and a 12-volt generator are very desirable to reduce power losses in rheostats. In chromium plating it is desirable to

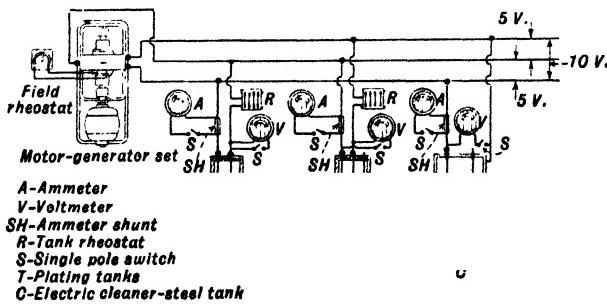


FIG. 41. A three-wire system for electroplating. (*Courtesy Chas. F. L'Hommedieu and Sons Company.*)

have a separate generator for each tank, because close control of the current is very necessary. Some generators are built with double commutators so that a three-wire system of distribution may be employed. A diagrammatic illustration of a three-wire system is shown in Fig. 41. Such a double commutator generator may, for instance, deliver 2,000 amp. at 6 volts or 1,000 amp. at 12 volts.

Stationary rectifiers are coming into use in the electroplating industry and are made in units up to 10,000-amp. capacity. The principal types now available are the copper oxide, copper sulphide, and selenium sulphide rectifiers.

Where but a small amount of plating is desired, storage batteries may be used, as in gold, silver, or platinum plating.

Current Distribution. The current is carried from the generator to the plating tanks over bus-bars, usually having a rectangular section. Copper bars, on account of their high conductivity, are used almost universally. They are manufactured in flat bars, $\frac{1}{4}$ in. thick and 1 to 4 in. wide. For short runs of 20 ft. or slightly over, the bars should have a cross-sectional area of 1 sq. in. for each 800 to 1,000 amp. For longer runs the cross-sectional area should be increased. For a tank 20 ft. from the generator requiring 40 ft. of conductor, there will be a voltage drop of over 0.3 volt for each 1,000 amp. per sq. in. If the bus-bars available have not sufficient current-carrying capacity, several bars may be bolted together so that they carry the current in parallel. The bars may be purchased in convenient lengths, and the ends can be bolted together to obtain any length desired.

For chromium plating it is desirable to have a separate generator for each tank, with a rheostat in the field circuit of the generator so that the voltage and therefore the current density in the plating tank can be closely regulated. A 12-volt generator seems to be desirable, but several plants operate successfully with a 6-volt generator.

For other plating tanks it is satisfactory to feed all tanks from the same conductors with a rheostat in series with each tank. Figure 42¹ shows a series rheostat in which a number of resistance coils are connected in series. The coils are introduced into the circuit one after another, so that the total resistance is equal to the sum of all the coils in the circuit. In the parallel rheostat, shown in Fig. 43,¹ any coil or any combination of coils can be used. The parallel rheostat therefore has greater flexibility than the series rheostat. As more coils are connected in the parallel rheostat, the greater the current that passes through the

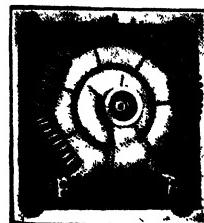


FIG. 42. A series rheostat.¹

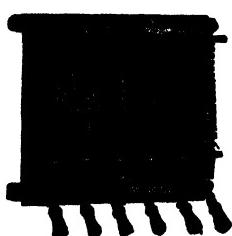


FIG. 43. A parallel rheostat.¹

¹ The illustrations of series and parallel rheostats were selected because they show clearly the arrangements of the resistance coils. Present-day rheostats, although constructed on the same principle, are partly or fully enclosed and have improved contacts to lessen the electrical resistance.

plating tank. In order to provide for the greatest flexibility the coils should have progressively increasing resistance, as for instance, 0.01, 0.02, 0.03, 0.04, 0.05 ohm, respectively. A parallel rheostat with coils having resistances as indicated would give a minimum current of 120 and a maximum of 1,370 amp. on a 6-volt line. However, for ease of regulation it is desirable to have the resistance coils in such ratios that the current passed by the individual coils will have the ratio 1, 2, 2, 5, and 10.

Rheostats are supplied in sizes ranging from a maximum load of 15 amp. for the small ones to about 7,500 amp. for the large ones. The larger sizes are expensive and inefficient, for they in no way reduce the power required to operate the generator.

Electrical Measuring Instruments. In electroplating, the current density has an important bearing on the character of the plated deposit, so that it is important to know what the current through the tank is. For articles of regular shape it may be easy to determine the area fairly accurately, and with the aid of an ammeter it is then a simple matter to adjust the current properly. For articles of irregular shape, it may be impossible to calculate the plating area even approximately. It may then be necessary to depend upon a voltmeter for the proper information for regulating the current. If, for example, in a nickel-plating bath it is desired to run at a current density of 6 amp. per sq. ft., it is often assumed that, if a flat sheet of 1 sq. ft. is placed in the tank as cathode and the current is adjusted to give 6 amp., the same voltage reading will thereafter give the desired current density regardless of the size or shape of the articles to be plated. This is true approximately only if the composition and temperature of the solution remain constant and if there is no change in the anode polarization.

Tanks. Wooden tanks are commonly used for rinse tanks, steel for cleaners and alkaline solutions, and lead-lined steel tanks for baths containing sulphuric or chromic acid. Rubber-lined tanks are used for neutral and acid baths, such as acid pickles, acid copper and zinc solutions, and nickel solutions. Soapstone, hard rubber, glass, and enameled iron have also been used for tanks, especially for the smaller sizes.

Agitation and Motion Plating. In some electroplating processes it is desirable to agitate the solution. Agitation serves to keep the composition of the solution more uniform and thereby permits the use of a greater current density.

Agitation by means of air is one of the simplest forms available. The air is generally introduced through a perforated lead or Ever-dur grid or pipe, the rising bubbles of air keeping the solution constantly in motion.

Air agitation is used in electrotyping but not very extensively in electroplating. It serves to stir up sediment and may thus cause rough deposits. In acid copper baths it fosters the formation of excess copper sulphate but permits the use of a higher current density and produces dense copper deposits. In cyanide solutions, air agitation increases the formation of carbonates and is therefore undesirable. In lead, zinc, and nickel plating, air agitation is of doubtful value if not actually undesirable.

A very satisfactory method of obtaining agitation is by a method called barrel plating. A simple form of plating barrel is shown in Fig.

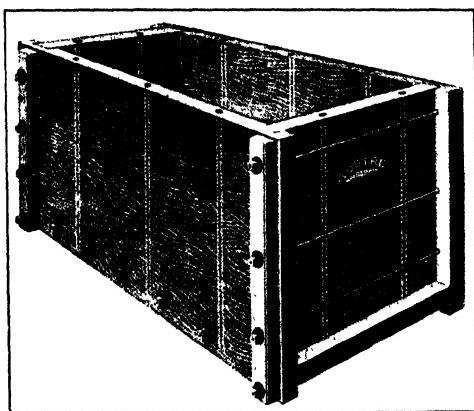


FIG. 44. A wooden plating or rinsing tank. (*Courtesy The Lustre Company.*)

45, consisting of an open cylindrical tank rotating about its axis, which is inclined at an angle of about 45° . The articles are plated in the barrel, making contact with the negative terminal by means of metal bars attached to the inside of the barrel. The main disadvantages of such a barrel are that the anode area is small and the solution must be emptied from the barrel in order to remove the work. Simplicity of construction is in favor of this type of barrel.

Another type of plating barrel and one which is in more common use is a horizontal perforated cylinder containing the work to be plated. The cylinder revolves in the plating solution in the tank and may be lifted from the solution for discharging and charging. The cylinder is made from some non-conducting material such as wood, celluloid, hard rubber, or formica. The perforated drum increases the resistance so that 10 or 12 volts may be necessary instead of half that amount in ordinary plating. To decrease the resistance, the plating solution is usually prepared with a higher metal content than for still plating.

Both types of plating barrels are especially used for plating small articles such as nuts, bolts, and screws. The tumbling of the load has a gentle abrading and polishing action. The motion of the barrel at the same time agitates the solution.

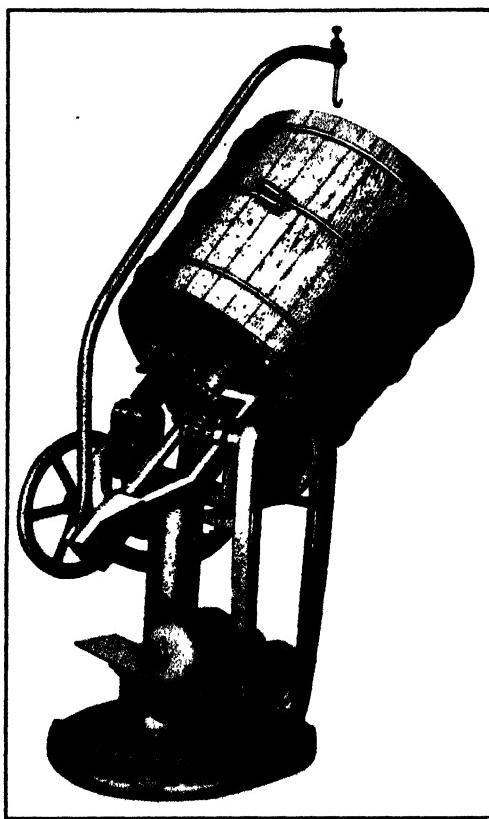


FIG. 45. An oblique plating barrel used for plating small objects. (*Courtesy Chas. F. L'Hommedieu and Sons Company.*)

In a rotary plater the ware to be plated is suspended from a wheel or spider rotating slowly in a horizontal plane above the tank, as shown in Fig. 46. The inner row of anodes also rotates but in the opposite direction; the outer ring of anodes is stationary. In another form an elongated rectangular tank is used with a conveyor above the tank carrying the load around the tank.

In large-scale production this conveyor plating machine has developed into various types of automatic plating machines, one kind of which is shown in Fig. 47. Such machines may be constructed to clean, pickle,

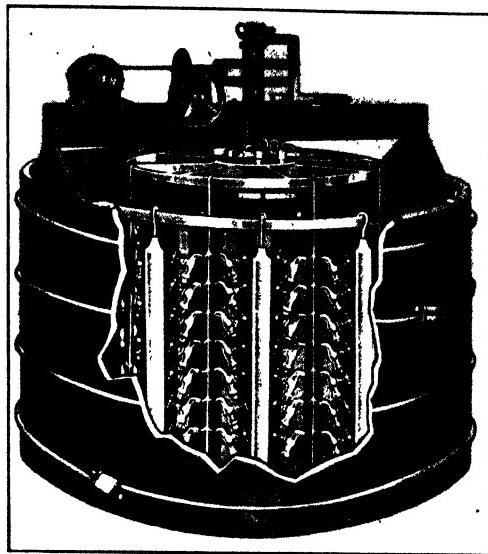


FIG. 46. A rotary plater. (*Courtesy Lasalco, Inc.*)

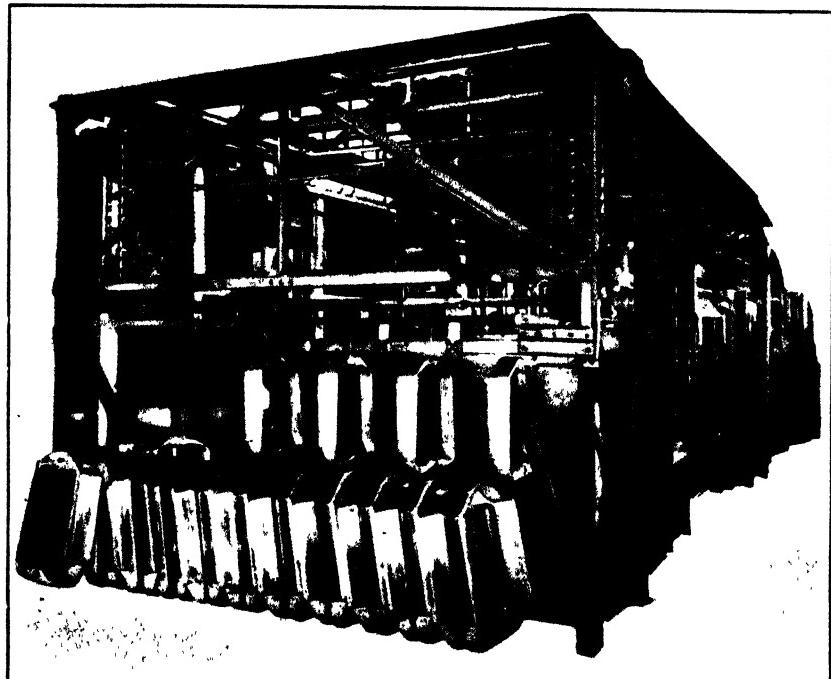


FIG. 47. Loading end of a full automatic plating machine. (*Courtesy The Meeker Company.*)

plate, and dry the ware automatically. A diagrammatic plan view of one type of automatic plating machine is shown in Fig. 48.

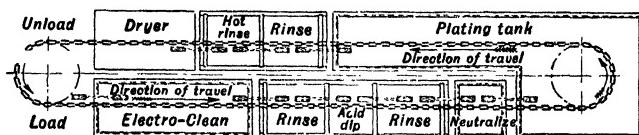


FIG. 48. Plan view of a plating machine. (Courtesy The Meeker Company.)

Circulation and Filtration. The anodes used in plating are not pure, and sludge will gradually accumulate at the bottom of the tanks. Some sludge will remain in suspension, especially in tanks in which some form of agitation is used. It is therefore necessary to filter the plating solution from time to time and to remove any sludge. The plating solution is therefore pumped through a suitable filter. One type of filter is constructed like the conventional filter press, with bronze in those places where the solution comes in contact with the metal. If a number of tanks contain like solutions the solutions may be continually circulated through all the tanks and through a filter.

CLEANING ARTICLES TO BE PLATED

In all types of electroplating, it is important that the base metal to be plated is absolutely clean. The cleaning process resolves itself into two major operations: (1) removal of greasy materials, and (2) removal of scale.

Removal of Greasy Materials. Nearly all metallic surfaces, unless they have been recently cleaned, contain some greasy material. This may be grease or oil added during a machining, stamping, or polishing process, or that added to avoid rusting during storage; or it may be accidental grease from the hands or clothing of workmen. If the grease is an organic one, it may be converted into a soluble soap by the action of an alkali, and the removal of such greases is a relatively simple process. Petroleum oils are not saponifiable and must be removed by solvents or other means. The removal of greases may be accomplished by the following means:

(a) *Use of Organic Solvents.* The article to be cleaned may be washed with gasoline, benzene, or carbon tetrachloride. Gasoline and benzene are used more commonly because they are cheap, but on account of their fire hazard and the toxic properties of benzene (benzol) their use should be limited. Carbon tetrachloride is excellent but its high price limits its extended use.

Vapor-phase degreasing is finding considerable application. The article to be cleaned is suspended in the vapors of the boiling solvent; the vapors condense on the object, and the condensed vapors wash off

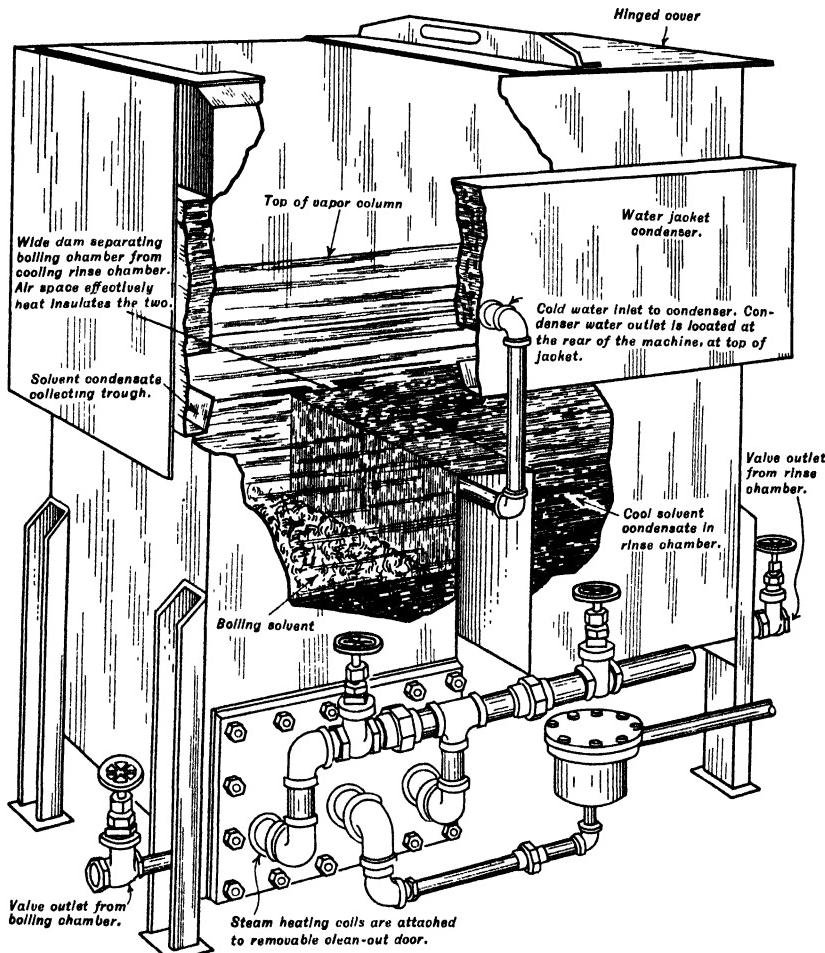


FIG. 49. Sectional view of a vapor-phase degreasing machine.

greasy materials and then drop back into the liquid below. Fresh vapors continue the washing process, and usually the cleaning is complete in a few seconds. The solvent should be one that produces a heavy vapor to keep evaporation losses at a minimum, should have a low latent heat of vaporization for quick condensation, and should be non-inflammable. Trichloroethylene is a suitable solvent for this purpose. A vapor-phase degreasing unit is shown in Fig. 49. The water

jacket serves to reduce evaporation losses. When the solvent becomes loaded with grease it is distilled and used again.

(b) *Use of Alkaline Solutions.* Greases can be emulsified by hot alkaline solutions, and then washed from the metallic surface. Such an emulsifying agent may be a solution of sodium hydroxide, sodium carbonate, or soap. Electroplating establishments generally buy "metal cleaners" prepared in drum lots. Such cleaners usually contain two or more of the following ingredients: sodium carbonate (soda ash), Na_2CO_3 ; sodium carbonate (sal soda), $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; sodium hydroxide, NaOH ; trisodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$; sodium silicate, Na_2SiO_3 ; sodium cyanide, NaCN ; and borax, $\text{Na}_2\text{B}_4\text{O}_7$. The addition of finely divided solid particles, as of silica, infusorial earth, carbon, etc., is also helpful; their action appears to be one of gentle mechanical abrasion and of absorption.

(c) *Use of Electrolytic Cleaning Processes.* The article to be cleaned may be made a cathode in a tank containing an alkaline solution. A high current density 30 to 35 amp. per sq. ft. is used, and there is a brisk evolution of hydrogen on the article to be cleaned. The cleaning action is probably a combination of a "lifting" process by the fine gas bubbles, and the formation of free alkali at the cathode surface. The tank is usually of iron and is made the anode; the solution should be heated above 50° C. (122° F.); a boiling temperature is used in many plants. A cleaning operation of a few minutes is ordinarily sufficient.

If articles containing zinc, tin, lead, or solder are cleaned in an electrolytic cleaner, these metals may pass into solution, and later be plated as a thin film on the article being cleaned. Such a film should be removed by reversing the current for a few seconds so that the cleaned article becomes anode.

An electrolytic cleaning solution may consist of:

	g./l.	oz./gal.
Sodium carbonate, Na_2CO_3	50	6.7
Sodium hydroxide, NaOH	15	2.
Sodium cyanide, NaCN	10	1.3

A solution has been developed by Watts² in which cleaning and copper plating are carried on in the same solution. The composition of the solution is similar to that of a copper cyanide plating solution, but the copper content is lower and the free cyanide content higher. The solution is used at a temperature of 80° C. (176° F.) or higher. The anodes are of iron so that copper salts must be added from time to time. When a greasy or oily piece of iron or steel is made cathode in the solution, the

² O. P. Watts, *Trans. Am. Electrochem. Soc.*, 27, 141 (1915).

grease is removed largely by the mechanical action of the liberated hydrogen, which will also reduce small rust areas. As soon as clean metal is exposed, copper plates on it.

Removal of Scale and Other Oxides. All materials requiring plating on a commercial scale will have a thin film of metallic oxide on the surface unless the surface has been well covered with an oil or grease, but even then, scale may have been formed before the protecting coat has been applied. Several methods are available for the removal of scale.

(a) *Pickling Iron and Steel.* In the pickling of ferrous articles, sulphuric and hydrochloric acids are commonly used. Hydrochloric acid is preferable for it acts more quickly than sulphuric, but its greater cost makes it give way to sulphuric acid in most cases. The action of the acid on scale is a combination of solution of the scale and a mechanical separation due to the formation of bubbles of hydrogen between the scale and the metal as the acid attacks the metal. Iron castings and steel that has been sand-blasted may have small grains of sand imbedded in the surface; these can be removed by the use of hydrofluoric acid. In the pickling with hydrochloric or sulphuric acid some of the hydrogen liberated is absorbed by the iron or steel and causes a temporary brittleness until the hydrogen has escaped to the air. The ferrous sulphate formed during the pickling process with sulphuric acid is not of sufficient value to warrant its recovery, and city ordinances usually forbid running the spent acid into the sewers, so that, in large establishments requiring a great deal of pickling, the disposition of the spent acid may be a big problem.

Suitable concentrations of acids for pickling purposes are shown in Table XIII.* All the values given are approximate.

TABLE XIII
CONCENTRATIONS OF PICKLING SOLUTIONS

Acid	Nor-mality	Per Cent Acid by Weight	Grams Pure Acid per Liter	Pints Commercial Acid per Gallon Water	Pounds Commercial Acid per Gallon Water
Sulphuric, H_2SO_4	2	10	100	0.5	1.
Hydrochloric, HCl	2	7	73	1.25	1.5
Hydrofluoric, HF	2	4	40	0.5	0.7

(b) *Electrolytic Removal of Scale.* If iron or steel is coated with a thin layer of scale, the article may be made the cathode in a 30 per cent

* W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming*, second edition, p. 150, McGraw-Hill Book Company, New York, 1930.

solution of sulphuric acid heated to 60° C. (140° F.). The scale is reduced to iron, and there is little loss of the metal, but the absorbed hydrogen makes the metal brittle. The iron may be made the anode in the same bath; then there is no impairment of the physical properties of the iron, but there is loss of metal.

A special electrolytic descaling process⁴ has been developed in which the clean descaled metal is covered with a thin layer of lead or tin. This lead or tin may easily be removed prior to subsequent plating or other type of finishing, but it serves as a protective coating during storage. The article to be descaled is first treated for removal of oil or grease by one of the methods previously discussed, unless this step is unnecessary. It is then placed as cathode in the descaling electrolysis cell. The electrolyte consists of a 10 per cent by volume sulphuric acid solution and is operated at 60 to 71° C. (140 to 160° F.) and at cathode current densities ranging from 4.3 to 10.7 amp. per sq. dm. (40 to 100 amp. per sq. ft.). If the protective film is lead, lead anodes are used in the cell and a small amount of sodium chloride or hydrochloric acid is added to the electrolyte to increase the anode corrosion. If the protective coating is tin, approximately 98 per cent of the anode surface is supplied by Duriron anodes and the remaining 2 per cent by tin anodes. There is also added to the electrolyte about 22.4 g. per liter (3 oz. per gal.) of Glauber salts, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, to increase the conductivity and 0.75 g. per liter (0.10 oz. per gal.) of glue for brightening. The Duriron anodes become coated with a thin porous silica diaphragm, thus preventing the ferrous iron in the bath from being oxidized to ferric iron. Ferric ions slow up the operation of the process, but ferrous ions do not.

The action of the descaling process is to "blast" off the scale through the copious liberation of hydrogen at the cathode and immediately to deposit on the clean surface a thin, dense, and adherent metal film.

The high overvoltage of hydrogen on lead or tin endows the process with good throwing power, causing the intensity of the hydrogen evolution to shift automatically from descaled and plated areas to more remote areas not yet descaled. The hydrogen evolution therefore progresses to the most remote or recessed parts. During this process, the already descaled and plated parts receive a further deposit of metal, but, at the pH of the bath and the current densities employed, this additional deposit is spongy. The time of descaling ranges from 3 to 10 minutes, depending upon the nature of the metal or alloy and the thickness and tenacity of the scale.

⁴ T. E. Dunn (The Bullard Company), Electrolytic Method of Cleaning Metal, U. S. Patent 1,775,671, Sept. 16, 1930; C. G. Fink and T. H. Wilber, *Trans. Electrochem. Soc.*, 66, 251 (1934).

If it is desired to remove the protective film before drying, the work is placed as anode in a reversed alkaline bath containing approximately 90 g. per liter (12 oz. per gal.) of caustic soda and one-third the amount of trisodium phosphate, Na_3PO_4 . The bath is used boiling hot, and it quickly strips the lead or tin from the work. After the metal film has been removed the work is washed and dried.

(c) *Sand Blasting.* Castings may be cleaned by means of a sand blast. A spray of sand or steel shot is blown against the casting with a blast of air, which removes the scale mechanically. In many of the smaller plants the sand blast is used in a small room, the men wearing goggles and aspirators. But even with the utmost protection the fine silica dust will get into the respiratory system. It is desirable that sand blasting be done in a closed booth, the workman manipulating all phases from without. Sand blasting will affect the surface of the article to be cleaned, and is sometimes used as a finishing process where a matt surface is desired. If the air pressure is too great, some sand may be imbedded in the surface of the iron, and will have to be removed with hydrofluoric acid before the article can be electroplated.

(d) *Wire Brushes.* Wire brushes are very effective; they may be used alone, but preferably with an abrasive like pumice, silicon carbide, or emery, in connection with an alkaline solution.

(e) *Tumbling Barrels.* Small articles may be cleaned very effectively in tumbling barrels. The articles are put in a tumbling barrel with steel shot, sand, emery, or other suitable abrasive in a soap or other alkaline solution. These abrasives may be used wet or dry. Tumbling removes scale, rust, roughness, burrs, fins, wire edge, pits, and discolorations.

(f) *Cleaning Brass.* If a brass surface to be plated is fairly clean it can be prepared for plating by immersion in a "bright dip." Generally a "scaling dip" is first used to clean the metallic surface. This is followed by a bright dip to produce a final bright finish. The subject of dips for brass has been studied by Graham,⁵ and his results are given in Table XIV. Any oil or film of soap or cutting compound on the brass must first be removed in a hot sodium hydroxide solution or some cleaning compound. This is followed by a hot or cold water wash.

The bright dip solution should be kept below 35° C. (95° F.). Wood soot added to the dip aids in a uniform attack of the acid.

CONTROLLING THE NATURE OF ELECTRODEPOSITS

The smoothness, hardness or softness, and brightness obtained in electroplating are determined largely by the physical structure of the

⁵ A. K. Graham, *Trans. Am. Electrochem. Soc.*, **52**, 289 (1927).

TABLE XIV
FORMULAS FOR BRASS CLEANING SOLUTIONS

	Degrees Bé.	Sp. Gr.	Scaling Dip		Bright Dip	
			g./l.	cc./l.	g./l.	cc./l.
H ₂ SO ₄ , Comm'l...	66	1.84	700	380	800	435
HNO ₃ , Comm'l...	40	1.38	100	72	100	72
HCl, Comm'l.....	21	1.17	5	4	2.5	2
H ₂ O.....	444	444	491	491

deposited metal. Electrodeposited metals, like all other metals, are crystalline in structure, and the appearance and physical properties of the deposit are produced by differences in the size or shape of the crystals. Generally, the finer the crystals of the deposited metal, the smoother, stronger, and harder the metal will be. The characteristics of the deposits can be governed to a large extent by the proper control of a number of factors.⁶

Current Density. The current density in electroplating is expressed in amperes per square decimeter, or amperes per square foot:

$$1 \text{ amp. per sq. dm.} = 9.3 \text{ amp. per sq. ft.}$$

Increasing the current density, up to a certain point, increases the fineness of the crystals of the deposited metals.⁷ If the current density becomes too great, the metal ions near the cathode are removed so fast that the migration and diffusion of the ions do not supply fresh ones in sufficient quantities. There is then at the cathode an impoverishment of metal ions, and a rough, porous, or spongy deposit is produced with copper, or a cracked deposit with nickel. Black or spongy deposits are said to be "burnt." The average current density can be determined if the area of the exposed part to be plated is known, and if an ammeter is connected in series with the tank. It is good practice to have an ammeter, voltmeter, and variable resistance in connection with each plating tank. The marked evolution of hydrogen at the cathode usually indicates too great a current density for satisfactory metal deposition, a notable exception being the plating of chromium.

⁶ A more complete discussion is given in W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming*, second edition, p. 85, McGraw-Hill Book Company, New York, 1930.

⁷ A. Sieverts and W. Wippelmann, *Z. anorg. Chem.*, **91**, 1; **93**, 287 (1915).

Concentration and Agitation. The local impoverishment of metallic ions at the cathode, causing burnt deposits, can be alleviated by increasing the concentration of the metal salt in the bath. Not only are there more metal ions to start with, but also diffusion will proceed more rapidly if the metal-ion concentration does get low locally near the cathode; however, agitation will accomplish more rapidly what the diffusion of the ions would produce ultimately. Another effect of agitation is the sweeping away of gas bubbles from the cathode; this is especially marked in zinc plating. Agitation, however, is not used to any great extent in electroplating. The objections to agitation are: (1) Sediment is kept in suspension, and its lodging on the cathode causes rough deposits. (2) It usually decreases throwing power. (3) In cyanide solutions it favors the formation of carbonates. (4) In brass plating, it is harder to control the color of the deposited metal.

Temperature. Increasing the temperature of the electrolyte increases the coarseness of the crystals on the cathode. The size of the crystals deposited may be affected even by the seasonal changes in temperature. Since most plated work is expected to develop a high polish, it would appear that most electroplating solutions would be used cold, or as little above room temperature as possible. In spite of the tendency of hot solutions to develop a coarse plated structure, warmed baths are used commercially because other advantages accrue from their use. Heated solutions cause: (1) an increase in the solubility of the salts, which may permit the use of higher concentrations and therefore higher current densities; (2) an increase in the conductance, which reduces the tendency to treeing, lowers the cost of electrical energy, and causes a decrease in the crystal size; (3) a decrease in the occlusion of hydrogen, this decrease, in the case of iron and nickel, reducing the tendency to form cracked deposits.

Conductance. Good conductance reduces the voltage required for a given current density, and therefore is an economic advantage. Good conductance also reduces the tendency to treeing; this property is especially useful when it is desirable to form thick deposits.

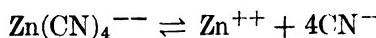
Metal-Ion Concentration. Where fine-grained deposits are desired, a low metal-ion concentration is desirable so that no one crystal can grow rapidly on account of the large number of ions ready to plate out on it. Small crystals produce bright deposits.⁸ The metal-ion concentration can be reduced by one or more of the following methods:

(a) *Use of a Dilute Solution.* A dilute solution will naturally reduce the number of ions in the electrolyte, but after the passage of a current there would be an impoverishment of ions at the cathode, and as a conse-

⁸ W. E. Hughes, *Metal Industry*, London, 25, 25, 49, 103 (1924).

quence a burnt or spongy deposit would result; therefore, this is not a practical method for reducing the metal-ion concentration.

(b) *Use of a Complex Salt.* In a cyanide zinc solution, the dissociation is as follows:



In the first equation, no zinc ions are formed. In the second, zinc ions are formed but only to a slight extent. As fast as any of the zinc ions plate out, more are formed from the ever-ready complex ions, $\text{Zn}(\text{CN})_4^{--}$. In zinc and copper cyanide solutions, therefore, there exists one ideal condition; there is a low metal-ion concentration, yet there will be no depletion of these ions, for they are formed as fast as they are removed.

(c) *Use of a Common Ion.* The metal-ion concentration can be reduced by the addition of a compound with a common ion. The number of copper ions in a copper sulphate solution can be decreased by adding sodium sulphate. It is possible to reduce the metal-ion content of a normal salt solution to one-tenth its original value by the addition of a common ion. Though the reduction of ions is not as marked as in cyanide solutions, it is enough to produce a noticeable effect on the deposited metal.

Hydrogen-Ion Concentration. In nickel-, zinc-, and iron-plating solutions, a high acid content (and therefore a low pH value) causes a fine and therefore bright deposit. In a nickel-plating solution free from addition agents, a bright deposit may serve as a warning that the solution is near the danger point at which cracked or curled deposits will occur.

Since the metals at the top (negative end, Table VII, p. 38) of the electromotive series are more active chemically than those lower in the series, it would appear that they would plate out of the solution with more difficulty. With special reference to hydrogen, if hydrogen ions are present in an electrolytic bath, they should plate out more easily than the ions of any metal above hydrogen. In broad general terms this is true. The overvoltage of hydrogen on zinc, however, is sufficiently high to permit zinc to be plated out unless hydrogen ions are present in relatively large numbers, that is, unless the solution is very acid. The overvoltage of hydrogen on iron and nickel is low, and they must be plated out from nearly neutral solutions. Copper, being below hydrogen in the series, can be plated from a solution of high acidity. Broadly

speaking, this would be true of all metals below hydrogen in the electro-motive series. Gold and silver, however, cannot be plated from acid solutions to produce deposits satisfactory for general electroplating.

Addition Agents. Addition agents are substances added to an electrolytic solution in addition to those main constituents whose functions are clearly understood. Addition agents produce no marked effect on the conductance or on the metal and hydrogen-ion concentrations of the solution, but they do influence the nature of the deposit. Nearly all addition agents are colloids or reducing agents. Common ones are glue and glucose, but a large number are in use, among which are quinine, peptone, and oil of cloves. The addition of too much colloid may produce a brittle deposit.⁹ The useful action of addition agents is mainly in reducing treeing and in causing the metal to be deposited in small crystals. Many, if not all, reducing agents act through the production of colloids. During the deposition, some of the colloidal material is deposited with the metal. However, the whole subject of the nature of the action of reducing agents is not fully understood. The development of solutions for bright plating has added new importance to the use of addition agents. Such solutions have come into wide use especially in the plating of nickel, copper, cadmium, and zinc. The procedure greatly reduces or eliminates the cost of buffing of the metal, conserves metal, and avoids reduction in the thickness of the plate.

Structure of Base Metal. It has been demonstrated especially by Hogaboom¹⁰ and others¹¹ that the structure of the base metal may have a marked effect on the characteristics of the deposited metal. This subject is still a large field for investigation.

Throwing Power. When a cathode of irregular shape, especially one with deep recesses, is being plated, the parts near the anode will be plated more heavily than will those farther away because, according to Ohm's law, there will be less resistance between the anode and the near parts of the cathode than between the anode and the far parts. The distribution of the deposits on the near and far parts of the cathode calculated on the basis of Ohm's law is called the "primary current distribution." In many practical electroplating operations this tendency toward uneven deposition is counteracted by other factors in favor of a more uniform distribution. A solution in which conditions are such as to correct to a fair extent such uneven distribution as would be obtained if Ohm's law were entirely applicable is said to have "good throwing power." One in which

⁹ R. Marc, *Z. Elektrochem.*, **19**, 431 (1913).

¹⁰ G. B. Hogaboom, *J. Am. Electroplaters' Soc.*, July, 1921.

¹¹ W. Blum and H. S. Rawdon, *Trans. Am. Electrochem. Soc.*, **44**, 305 (1923).

the distribution is that predicted by calculation is said to have no throwing power. Some solutions, like chromium-plating solutions, have a negative throwing power.

When a point on the cathode relatively near to the anode receives a greater current density than the other parts there is soon a greater reduction in metal ions at that point. This causes polarization, which produces a local back e.m.f. having the same effect as if the resistance were increased between the anode and the near point of the cathode. Consequently, the more remote parts receive more current than they would otherwise; in other words, the throwing power has been improved. If such polarization did not exist, the near point on the cathode would grow rapidly, every bit of metal deposited would aggravate the matter, and "treeing" would result. In solutions with high conductance, the relative effect of polarization is more pronounced, so that high conductance is said to improve the throwing power. Warming the solution also improves the conductance, but it reduces the effect of polarization still more, so that generally an elevation in temperature decreases the throwing power.

Methods for determining quantitatively the throwing power of solutions have received much study in the past years, especially by Haring and Blum¹² and by others who have developed modifications of their processes.

¹² H. E. Haring and W. Blum, *Trans. Am. Electrochem. Soc.*, **44**, 313 (1923); H. E. Haring, *ibid.*, **46**, 113 (1924).

CHAPTER VI

ELECTROPLATING SOLUTIONS

This chapter is devoted to a brief discussion of some of the more common plating solutions as well as a few of the solutions not so widely used. For a more complete discussion of electroplating the reader is referred to books¹ and periodicals² devoted fully or partly to that subject.

Copper-plating solutions will be discussed first because a discussion of them introduces principles applicable to many other plating solutions. The remainder of the plating solutions will be taken alphabetically for the sake of convenience in reference. Some alloys are discussed in connection with one of the chief metals in the alloy; others are treated separately at the end of the chapter.

Copper Plating. Practically all commercial copper plating is done in one or both of two types of solutions. One of these invariably contains copper sulphate and sulphuric acid and is called the acid copper sulphate solution, or more briefly, the acid sulphate bath; the other solution contains no acid, but in addition to copper ions contains also cyanide ions and is generally called the cyanide bath or the alkaline bath. Each of these solutions has special uses.

Copper Acid Solutions. The copper acid bath is one of the simplest the electroplater encounters. It is not suitable for plating directly on iron, or on metals above iron in the electromotive series. For copper plating on iron it is necessary first to plate a thin layer of copper from a cyanide bath, and then to finish the plating from the acid bath. The two main constituents of the acid copper sulphate bath are sulphuric

¹ *Modern Electroplating*, The Electrochemical Society, Columbia University, New York, 1942; W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming*, second edition, McGraw-Hill Book Company, New York, 1930; B. Freeman and F. G. Hoppe, *Electroplating with Chromium, Copper, and Nickel*, Prentice-Hall, New York, 1930; G. Langbein and W. T. Brannt, *Electro-Deposition of Metals*, eighth edition, H. C. Baird and Company, New York, 1924; E. S. Richards, *Chromium Plating*, J. B. Lippincott Company, Philadelphia, 1936.

² *Transactions of the Electrochemical Society* (called *Transactions of the American Electrochemical Society* prior to November, 1931), Columbia University, New York; *Monthly Review of the American Electroplaters' Society*, Chicago; and *Metal Cleaning and Finishing*, Pittsburgh, Pa.

acid and copper sulphate, the latter obtained commercially as the crystallized salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), containing 25.4 per cent copper when pure.

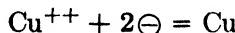
Copper sulphate, a by-product obtained in the electrolytic refining of copper, is pure enough for electroplating use, although it contains small amounts of arsenic, iron, zinc, and other impurities.

Sulphuric acid is sufficiently pure in the commercial grade, but it too contains impurities, such as arsenic, iron, chlorides, nitrates, and organic matter. As will be shown later, in acid copper sulphate baths, copper sulphate is being manufactured at the expense of the sulphuric acid, so that it is necessary to remove the excess sulphate and to replenish the acid. It is therefore more important to employ fairly pure acid than to start with pure copper sulphate.

The functions of sulphuric acid in a copper sulphate plating bath may be summarized as follows:

1. It prevents the hydrolysis of cuprous sulphate and subsequent formation of basic salts. As will be shown later, the cuprous sulphate is formed in the process of electrolysis.
2. It increases the conductivity of the bath. A copper sulphate solution containing 150 g. of the crystals per liter has a resistivity of 29 ohm-cm. If 50 g. per liter sulphuric acid is added the resistivity drops to 5.3 ohm-cm., and with 200 g. per liter the resistivity drops to 1.8 ohm-cm. This increase in conductivity: (a) reduces the cost of power required, and (b) reduces the formation of rough and treed deposits at high current densities.
3. It decreases the copper-ion concentration without decreasing the potential supply of copper ions.

The theoretical and simplest cathode reaction is:



That is, copper ions in contact with the cathode receive two electrons each from the circuit, and plate out on the cathode. At the anode, the reverse is true:

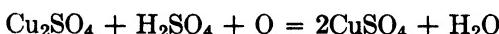


Copper atoms in the anode, in contact with the electrolyte, surrender two electrons each to the circuit and pass into solution as ions. The sulphate ions, SO_4^{--} , and hydrogen ions, H^+ , take no part in the electrochemical changes, and if the two reactions mentioned above were the only ones, there would be just as much copper going into solution as is plated out, and as a consequence the copper sulphate and sulphuric acid contents would remain constant. Actually, however, the copper

sulphate content increases, and the sulphuric acid content decreases. This is due to the fact that copper may have a valence of 1 or of 2, Cu^+ , and Cu^{++} . Therefore, some of the anode copper goes into solution as cuprous ions:



The cuprous ions thus formed require only half the current that the formation of cupric ions requires. If these cuprous ions would reach the cathode and be plated out as such, there would be no change in the copper sulphate content of the bath. The cuprous ions, however, tend to become oxidized to cupric ions:



or



The oxygen is derived from oxygen dissolved in the solution, which is particularly true when air agitation is used during plating. In addition, cuprous ions are oxidized as follows:



or

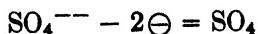


The metallic copper thus formed settles to the bottom and becomes part of the anode sludge.

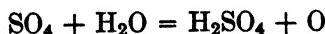
The excess copper sulphate formed must be removed from the bath; this can be accomplished by any or all of the following methods:

(a). Periodically some of the bath is removed and replaced with water and sulphuric acid to bring the bath back to the desired concentration. The removed solution can be evaporated in lead-lined tanks and the copper sulphate recovered. In small plants the cost of the evaporation is usually more than the value of the recovered copper sulphate.

(b) The copper anodes are replaced to a certain extent with lead ones, so that the excess copper sulphate is removed and the acid is regenerated. The anode reaction on the lead is:



and



The oxygen first attacks the lead anodes to form a layer of lead peroxide, PbO_2 , after which the oxygen escapes to the air carrying along an objectionable fine spray of solution. The lead peroxide formed on the anode causes increased polarization.

(c) The removed solution is thrown away; this is common practice in small plants, and in some large ones as well.

Acid copper sulphate baths are not suitable for direct plating on iron, as explained above, but Satka⁸ found that copper can be deposited directly on iron or steel from an acid bath if these metals are first dipped in a solution of arsenic trioxide in hydrochloric acid (60 g. As₂O₃ per liter of concentrated acid). The iron or steel becomes coated with arsenic, on which the copper from the acid bath plates in a firm deposit.

The big field for the acid copper bath is in electrotyping. It is also used in other types of electroforming, as in the production of tubes and floats, and for all electrolytic copper refining.

The copper anodes used in copper plating are either obtained from native copper, found almost in the pure state near Lake Superior, or from electrolytic copper, obtained from sulphide or other copper ores. Copper anodes from either source are about equally satisfactory. Copper anodes may be cast, rolled, or formed electrolytically. In cyanide solutions all types of anodes seem equally satisfactory, but in the acid sulphate bath the cast ones are least satisfactory.

1. COPPER ACID SOLUTIONS.

	g./l.	oz./gal.
Copper sulphate, CuSO ₄ ·5H ₂ O.....	150 to 240	20 to 32
Sulphuric acid, H ₂ SO ₄	45 to 100	6 to 13

Generally, the operating temperature is low, below 25° C. (77° F.), with a current density of 6 to 16 amp. per sq. dm. (56 to 150 amp. per sq. ft.) for hard deposits. For soft deposits the temperature should be higher, 35° C. (95° F.); the current density lower, 3 amp. per sq. dm. (28 amp. per sq. ft.); and the acid content should be lower, 45 g. per liter (6 oz. per gal.). Air agitation is commonly used for copper-acid baths.

A variety of addition agents are in use. Glue in a concentration as low as 3 g. per liter is effective in counteracting treeing and produces a smooth and hard deposit. Gelatin, goulac, casein, dextrose (as corn sugar, syrup, or molasses), urea, cresol, phenol, and others are in use.

Copper Cyanide Solution. Copper cyanide solutions contain sodium cuprocyanide, NaCN·CuCN or NaCu(CN)₂, as the essential constituent. The copper is in the cuprous state, Cu⁺, instead of in the cupric state, Cu⁺⁺, as in the acid sulphate bath. It makes no difference in the final solution whether the sodium cuprocyanide is dissolved as such or whether sodium cyanide, NaCN, and cuprous cyanide, CuCN, are used separately, provided that the purities are the same in both cases, and

⁸ J. Satka, *Monthly Rev., Am. Electroplaters' Soc.*, 5, No. 8, p. 5 (1918); O. P. Watts, *Trans. Am. Electrochem. Soc.*, 35, 265 (1919).

that the separate salts are dissolved in molecular ratios; the simplest method is to dissolve cuprous cyanide in a sodium cyanide solution.

Sodium cyanide is a white solid, preferably purchased in small lumps. On account of the poisonous nature of the salt, great care must be taken not to get any into the system. Care must also be taken not to let any cyanide come in contact with acids, for the hydrocyanic acid, HCN, formed is extremely poisonous, and on account of its volatility is particularly dangerous. Hydrocyanic acid when taken in sufficient doses is one of the quickest-acting poisons known. Commercial sodium cyanide is usually 95 to 98 per cent pure. When exposed to carbon dioxide gases, some of the cyanide is converted to sodium carbonate, so that the cyanide stored at the plant, unless sealed, will contain some sodium carbonate formed from carbon dioxide in the air. Potassium cyanide, KCN, was generally used instead of sodium cyanide before the first World War, but the sodium cyanide is cheaper. Cuprous cyanide, CuCN (generally called copper cyanide although there exists also cupric cyanide Cu(CN)₂), is white when pure; the commercial product is yellowish and contains about 70 per cent copper, instead of 71 per cent as in the pure product.

In addition to sodium and copper cyanide other substances are generally added on account of their beneficial effects, but their actions are not fully understood. Sodium carbonate is a common constituent in copper cyanide baths. It helps to keep the solution alkaline and thus prevents the formation of hydrocyanic acid by carbon dioxide from the air; i.e., it prevents the reaction

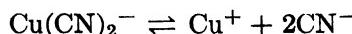


Sodium thiosulphate, Na₂S₂O₃, also called "hypo," added in small quantities acts as a brightener. Small amounts of lead acetate, Pb(CH₃COO)₂, or of sodium plumbate, Na₂PbO₂, also act as brighteners. The solution must contain some excess sodium cyanide (or potassium cyanide), for, since some cyanide is converted to carbonate by carbon dioxide from the air, the sodium cuprocyanide would decompose and cuprous cyanide and hydroxide would be precipitated. Excess cyanide also increases anode corrosion, for, whereas the anode corrosion in an acid copper bath may be above apparently 100 per cent efficiency, it is poor in a cyanide solution. Too much free cyanide, however, causes excess gassing of hydrogen at the cathode.

The sodium cuprocyanide dissociates to form sodium ions and a complex cuprocyanide ion:



The copper-containing ion dissociates further, forming copper and cyanide ions:



This second dissociation takes place to only a small extent, but, as fast as the copper ions are removed by plating out on the cathode, fresh copper ions are formed. It will be observed that the copper is univalent (Cu^+), and one would expect the plating from a copper cyanide bath to be about twice as efficient as plating from an acid copper sulphate bath where the copper is divalent (Cu^{++}); but, actually, the cyanide copper solution is less efficient than the acid copper solution; the current efficiency of the cyanide solution ranges from 80 down to 50 per cent. In addition to the low current efficiency, the power required to plate copper from a cyanide copper solution is greater than that required for an acid copper solution, for the resistance of the former is considerably higher than that of the acid solutions, and the anode and cathode polarizations are higher. The net result is that the power required to plate copper from a cyanide solution may be many times as high as from a sulphate solution.

Copper cyanide solution is used, therefore, only where it appears to be necessary. Its special field of usefulness is in plating copper directly on iron. Since copper is below iron in the electromotive series, the ions of copper will be replaced by metallic iron; that is, iron will precipitate copper ions out of solution and will itself go into solution as ions. In other words, the iron will be plated with a thin layer of copper, but the action will stop as soon as the iron is plated. This is called "deposition by immersion," and it takes place in the acid copper solution but not in the cyanide solution. The copper deposited by immersion is usually a spongy, poorly adhering coat, and, no matter how well the new layers of copper are deposited, the plating will be of little account if the layer next to the iron is non-adherent. Therefore, the cyanide solution is generally used for plating copper directly on iron. Since the protective action of copper from a cyanide solution is poor and the plating rate and efficiency are both low, the cyanide deposit is coated with copper from an acid copper bath, or with nickel, chromium, or other metal. Wernlund,⁴ however, has shown that under proper conditions cyanide solutions can plate copper on iron from start to finish, forming a hard, firm deposit. Cyanide copper deposits are also used in case hardening to protect the iron parts that are not to be hardened. It is likewise used as an under-coat for nickel and chromium plating, and especially on zinc and on die castings to prevent deposition by immersion in subsequent plating baths.

⁴ C. J. Wernlund, *Metal Ind.*, 26, 106 (1922).

2. COPPER ALKALINE SOLUTION.

	g./l.	oz./gal.
Cuprous cyanide, CuCN.....	22.5	3
Sodium cyanide, NaCN.....	30.0	4
Sodium carbonate, Na ₂ CO ₃	10.0	1.5

Temperature, 30 to 40° C. (86 to 104° F.).

Current density, 0.3 to 0.5 amp. per sq. dm. (2.8 to 4 amp. per sq. ft.).

Copper Rochelle Cyanide Solution. The copper cyanide solution described above has been in use for many years and is extensively used at present. However, a demand for a more efficient bath, and one from which heavier deposits could be plated satisfactorily, led to the development of a solution with a higher concentration of copper cyanide and relatively low free cyanide.⁵ Such a solution has also improved throwing power, but, when it was used with higher current densities, difficulties were encountered with anode performance. McCullough and Gilchrist⁶ recommended the use of Rochelle salt to improve the anode corrosion. Various other researches have led to the present Rochelle plating solution now widely used.

3. COPPER ROCHELLE CYANIDE SOLUTION.⁷

	g./l.	oz./gal.
Cuprous cyanide, CuCN.....	26	3.5
Sodium cyanide, NaCN.....	35	4.6
Sodium carbonate, Na ₂ CO ₃	30	4.0
Rochelle salt, KNaC ₄ H ₄ O ₆ ·4H ₂ O.....	45	6.0
Sodium hydroxide, NaOH, to give a pH of 12.6.		

Temperature, 50 to 80° C. (122 to 176° F.).

Current density, 2 to 6 amp. per sq. dm. (18.6 to 56 amp. per sq. ft.) for bright deposits.

The anode area should be at least double that of the cathode area, and iron anodes equivalent to about 5 per cent of the total area should be used. The anode efficiency ranges between 50 and 70 per cent; the cathode current efficiency, between 30 and 70 per cent, depending upon operating conditions.

Copper Oxalato Solution. On account of the poisonous nature of the copper cyanide solution, and on account of its instability, attempts have

⁵ L. C. Pan, *Metal Cleaning and Finishing*, 5, 152, 166 (1933); *Trans. Electrochem. Soc.*, 68, 471 (1935).

⁶ J. F. K. McCullough and B. W. Gilchrist, U. S. Patent 1,863,869, June 21, 1932.

⁷ A. K. Graham and H. J. Read, in *Modern Electroplating*, p. 188, The Electrochemical Society, Columbia University, New York, 1942.

been made to produce some other type of solution that would be more satisfactory. An essential requirement of such a solution would be a low copper-ion concentration. Fink and Wong⁸ have developed such a solution. The copper-carrying compound is disodium diaquodioxalato-cupriate, $\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$, which they call "oxalato." The conductivity of such a solution is very low so that sodium carbonate is added to increase the conductivity, and boric acid, H_3BO_3 , is added to act as a buffer.

Aluminum Plating. All attempts to plate aluminum from aqueous solutions, or from liquid ammonia solutions, have failed. Aluminum has been plated successfully from organic solutions, especially aluminum Grignard compounds (ethyl aluminum iodides) dissolved in dry ether, using aluminum anodes.⁹ Attempts have also been made to plate aluminum from fused electrolytes, but up to the present time aluminum plating has not attained commercial importance.

Antimony and Arsenic Plating. The electroplating of antimony and of arsenic has not reached much importance. Both metals have a grayish color and are used to some extent for producing antique or other decorative effects on trays, candy dishes, and a few other objects not exposed to the weather. Antimony is used mostly on copper, bronze, or brass, and gives a grayish color. Arsenic as plated from the solutions listed is darker in color. The solutions for both may be alkaline or acid. A few solution compositions are given below.¹⁰

4. ANTIMONY PLATING SOLUTION, ALKALINE.

	g./l.	oz./gal.
Antimony sulphide, red, Sb_2S_3	60	8
Soda ash, 58% light, Na_2CO_3	45	6

Temperature, 82° C. (180° F.).

Voltage, 1 to 2 volts.

Anodes, sheet steel.

5. ANTIMONY PLATING SOLUTION, ACID.

	g./l.	oz./gal.
Antimony chloride, SbCl_3	30	4
Hydrochloric acid, commercial, HCl	90	12

Temperature, 50° C. (120° F.) or less.

Voltage, 1 to 2.

Anodes, rolled nickel, or iron.

⁸ Colin G. Fink and C. Y. Wong, *Trans. Electrochem. Soc.*, **63**, 83 (1933).

⁹ D. B. Keyes and S. Swann, Jr., *Ind. Eng. Chem.*, **20**, 1068 (1928); *Univ. Illinois Eng. Expt. Sta. Bull.*, **206**, 10 (1930).

¹⁰ C. H. Proctor, *Metal Cleaning and Finishing*, **2**, 72 (1930).

6. ARSENIC SOLUTION, ALKALINE, BLACK TONE.

	g./l.	oz./gal.
Arsenious oxide, As_2O_3	75	10
Sodium hydroxide, 76% NaOH.....	37.5	5
Sodium cyanide, 98% NaCN.....	3.8	0.5

Temperature, about 18°C . (65°F .).

Voltage, 2 to 3.

Anodes, iron, carbon, or nickel.

7. ARSENIC SOLUTION, ACID.

	g./l.	oz./gal.
Arsenious oxide, As_2O_3	7.5	1
Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	7.5	1
Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	7.5	1
Hydrochloric acid, commercial HCl... .	60	8

Temperature up to 38°C . (100°F .).

Voltage, 1 to 2.

Anodes, steel, carbon, or nickel.

Cadmium Plating. Cadmium plating has come into considerable prominence in the last decade because it has made it possible to produce lustrous coatings of high protective value at low cost. The protective action of cadmium on iron and steel is excellent. According to some investigators the normal electrode potential of cadmium is below that of iron in the electromotive series, but there is not universal agreement on this matter. Experimental work ¹¹ indicates that in dilute salt solution cadmium and zinc behave alike in preventing corrosive attack on iron, and that under conditions normally encountered in commercial districts, and under normal atmospheric conditions, cadmium is electronegative to iron.

In general cadmium plate has quite a low resistance to chemicals, but it dissolves only very slowly in alkalies and is therefore used to protect washing equipment and steel imbedded in concrete. It is used on assemblies of dissimilar metals, such as steel and brass, to reduce voltaic-couple corrosion ¹² to a minimum, and it is used on a wide variety of hardware.

Cadmium-plating solutions, when properly prepared and operated, form deposits fairly free from porosity, even when plated in thin layers. Cadmium coatings above 0.0002 in. in thickness are practically non-porous. This is of special value in plating threaded parts, for no undercutting is necessary. For plating on brass, the thickness of the cadmium deposit is increased about 50 per cent.

¹¹ H. S. Rawdon, *Trans. Am. Electrochem. Soc.*, **49**, 339 (1926); C. M. Hoff, *ibid.*, **50**, 301 (1926).

¹² G. Soderberg and L. R. Westbrook, in *Modern Electroplating*, pp. 101-103.

8. CADMIUM PLATING SOLUTION.

	g./l.	oz./gal.
Cadmium oxide, CdO.....	30	4
Sodium cyanide, NaCN.....	100	13.2

Temperature, atmospheric.

Current density, 0.5 to 5.4 amp. per sq. dm. (5 to 50 amp. per sq. ft.).

During normal operation of the bath no attention is paid to the temperature except that in cold weather steam coils are used to bring the solution up to temperature. Barrel plating, which is ordinarily done with 12 volts, sometimes causes overheating and too rapid disintegration of the cyanide, so that the use of cooling coils may be desirable.

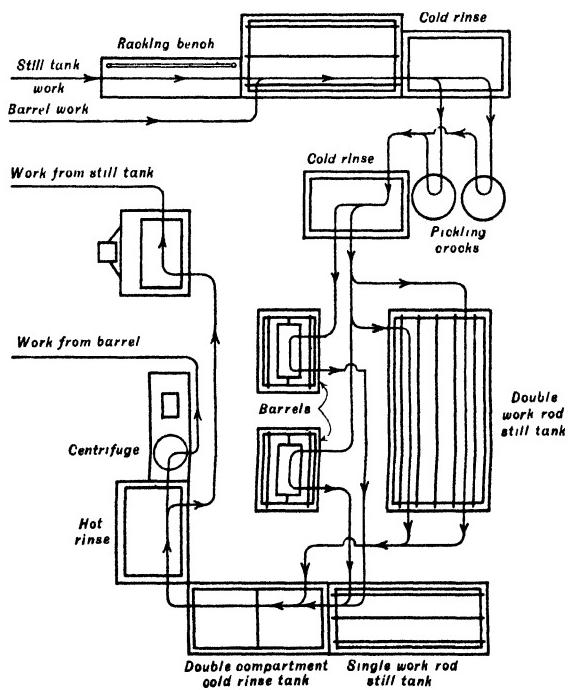


FIG. 50. Layout of a small electroplating plant.

Addition agents are usually employed to produce bright deposits. Among those suggested are glue, casein, goulac (wood pulp extract), turkon oil¹³ (sulphonated castor oil), instant Postum,¹⁴ and small

¹³ U. S. Patent 1,826,159 (The Grasselli Chemical Company).

¹⁴ U. S. Patent 1,692,240 (The Udylite Company).

amounts of nickel. A bright dip for cadmium consisting of chromic acid, CrO_3 , and a soluble sulphate has been described by Soderberg.¹⁵

In the Udylite process for cadmium plating,¹⁶ licenses are issued by The Udylite Company, Detroit, Michigan, to jobbing shops and manufacturing companies. Figure 50 shows a layout for a small Udylite plating unit. Figure 51 shows one of their patented ball anodes; the container, formed by a heavy helical coil, offers a simple method of renewing anodes. New balls are inserted in the top as the original balls dissolve in the solution and drop lower in the container; the anodic surface area remains constant.

In the Cadalyte process for cadmium plating,¹⁷ the ingredients for the electrolyte are supplied as a dry mixture by The Grasselli Chemical Company, Cleveland, Ohio. For use, the Cadalyte is dissolved, 2 lb. for each gallon of plating solution. This gives a solution of sp. gr. 1.146 (18.5° Bé.). The anodes, containing over 99.95 per cent cadmium, are also supplied by the company. A special type of anode has been developed which prevents loss of cadmium metal as scrap due to non-uniform solution, and yet permits an anode current efficiency of approximately 100 per cent. A current density of 1.1 to 4.3 amp. per sq. dm. (10 to 40 amp. per sq. ft.) may be used. Anodes and chemicals are likewise supplied for the Cad-A-Loy process in which cadmium alloys are deposited.

Chromium Plating. The electrodeposition of chromium is a relatively recent development, although deposits are recorded as having been obtained as far

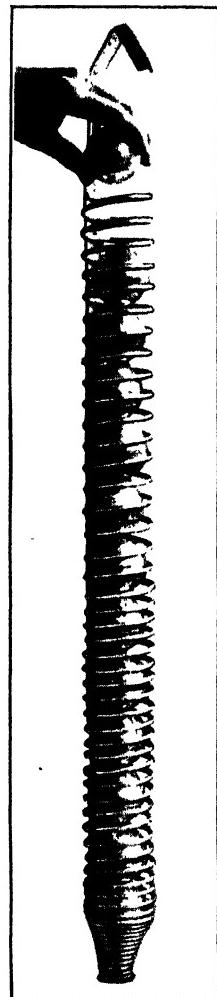


FIG. 51. Ball anode for cadmium plating. (Courtesy, The Udylite Company.)

¹⁵ G. Soderberg, *Trans. Electrochem. Soc.*, **62**, 315 (1932).

¹⁶ U. S. Patent 1,383,174-5-6 (1921) (The Udylite Company). Other patents assigned to the same company are U. S. Patents 1,504,298; 1,536,858-9; 1,537,020; 1,692,240; 1,537,046-7; 1,868,052; and Reissue No. 19,328.

¹⁷ L. R. Westbrook (The Grasselli Chemical Company), Cadmium plating, U. S. Patent 1,681,509, Aug. 21, 1928. Other patents assigned to the same company are U. S. Patents 1,564,413; 1,564,414; 1,681,509; 1,709,523; 1,818,179; 1,818,229; and 1,826,159.

back as the middle of the last century. Carveth and Curry¹⁸ in 1905 did some research on the subject and were followed by Sargent¹⁹ and Schwartz,²⁰ among others, and by Fink.²¹ Since then electrodeposition of chromium has reached great commercial importance.²²

It has found wide use as the finishing coat in the plating of automobile hardware and other parts requiring a bright finish and is used extensively for the plating of plumbing fixtures and a large variety of hardware and household appliances. On account of its hardness, chromium plating has found wide application where resistance to wear is important. It is used for plating the surfaces of dimensional gages, and on printing plates such as those for the printing of paper currency and postage stamps by the Government.²³ It will resist tarnishing in air at temperatures above 400° C. (752° F.). The plated metal has a low coefficient of friction.

Chromium resists oxidation and corrosion remarkably well at ordinary temperatures and is not acted on by nitric acid unless a halogen is present. Hydrochloric acid dissolves chromium freely, sulphuric acid more slowly; fruit acids have very little effect on it; sulphur compounds, practically none. One characteristic of electrodeposited chromium is that, under proper conditions, it can be deposited with a bright finish, requiring no polishing after plating.

At the present time, chromic acid, CrO₃, also called chromium trioxide, is used exclusively to supply the chromium ions. CrO₃ is more properly called chromic acid anhydride; on solution in water, it forms chromic acid:



This chromic acid dissociates to form hydrogen ions and chromate ions:



The exact nature of the phenomena which occur in the chromium-plating bath is not fully understood. The chromium in the H₂CrO₄ has a valence of 6, but at the cathode some of this is reduced to a lower

¹⁸ H. R. Carveth and B. E. Curry, *Trans. Am. Electrochem. Soc.*, **7**, 115 (1905); *J. Phys. Chem.*, **9**, 353 (1905); Carveth and W. R. Mott, *ibid.*, 231.

¹⁹ G. J. Sargent, *Trans. Am. Electrochem. Soc.*, **37**, 479 (1920).

²⁰ K. W. Schwartz, *ibid.*, **44**, 451–466 (1923).

²¹ C. G. Fink (Chemical Treatment Company, Inc., New York), Process of electrodepositing chromium and of preparing baths therefor, U. S. Patent 1,581,188, April 20, 1926.

²² For a review of the literature and a list of references see R. Schneidewind, Univ. Mich. *Eng. Research Bul.* **8** (1927) and **10** (1928). Modern commercial practice is given in *Circ.* **3** (1930).

²³ For a discussion of the applications of chromium plating see W. Blum, *J. Franklin Inst.*, **213**, 17 (1932).

valence by the hydrogen which is liberated. Part of the reduced chromium appears to react with the chromic acid to form what is called "chromium chromate," the composition of which has not yet been definitely established. However, in the operation of the process the reduced chromium compounds are oxidized at the anode to the hexavalent state (chromic acid).

CHROMIUM PLATING SOLUTIONS.

	g./l.	oz./gal.
9. Chromic acid, CrO ₃	250	33.5
Sulphate radical (SO ₄).....	2.5	0.33
10. Chromic acid, CrO ₃	400	53
Sulphate radical (SO ₄).....	4	0.53

Temperature for above baths, 40 to 55° C. (104 to 131° F.).

Current density, 10 to 25 amp. per sq. dm. (93 to 233 amp. per sq. ft.).

The sulphate radical may be supplied by sulphuric acid or by sodium sulphate. It may also be supplied by chromic sulphate, but difficulty is experienced in obtaining it in a pure form, and it is little used. The sulphuric acid and sodium sulphate, when pure, required for the above baths are as follows:

In plating solution 9, the 2.5 g. per liter of SO₄ will be supplied by 2.55 g. per liter (0.34 oz. per gal.) of sulphuric acid or by 3.7 g. per liter (0.49 oz. per gal.) of sodium sulphate. In solution 10, the 4 g. per liter of SO₄ will be supplied by 4.1 g. per liter (0.55 oz. per gal.) of sulphuric acid or by 5.9 g. per liter (0.80 oz. per gal.) of sodium sulphate. However, the chromic acid generally contains some sulphate, which should be determined and allowed for in adding the sulphuric acid or sodium sulphate.

To insure a bright chromium deposit and also maximum efficiency, the CrO₃ and SO₄ should be present in the bath and maintained in the approximate ratio ^{24, 25} of

$$\frac{\text{Weight of CrO}_3}{\text{Weight of SO}_4 \text{ radical}} = 100 \text{ or thereabouts}$$

The efficiency of plating is generally below 15 per cent.

For proper electroplating of chromium, the correlation and control of solution composition, temperature, and current density are very important. When the CrO₃ and the SO₄ in the bath are in the proper proportion, satisfactory plating can be obtained in most baths at temperatures

²⁴ H. E. Haring and W. P. Barrows, *Natl. Bur. Standards Tech. Paper* 346, 1927.

²⁵ J. W. Cuthbertson, *Trans. Electrochem. Soc.*, 59, 401 (1931).

ranging from 40 to 55° C. (104 to 131° F.), but the proper current density must be maintained for the particular temperature employed. If the current density is low, the deposit is milky; if high, the deposit is frosty. The current density half way between the limits of milky and frosty deposits, that is, half way between the limiting current densities, will produce a bright deposit. For baths 9 and 10 operated at 45° C. (131° F.), the current density for bright deposits on copper or brass is 16 amp. per sq. dm. (150 amp. per sq. ft.). In the plating of chromium on copper or brass, it is desirable that the introduction of the cathode close the plating circuit to prevent an attack on the metals by the chromic acid.

The throwing power in chromium plating solutions is poor, and difficulty may be experienced in obtaining a uniformly smooth deposit on some irregularly shaped articles. If the overvoltage of hydrogen on the metal to be plated is high, irregularly shaped articles can be plated more readily with a bright deposit than if the overvoltage is low. Recessed articles of copper or brass can be plated with a uniformly bright chromium deposit more easily than those of nickel or steel. If the cathode is introduced into the bath in such a manner that its immersion closes the plating circuit, the throwing power is improved on metals like nickel and iron which have a tendency to become passive in the chromic acid bath. Throwing power can sometimes be improved on such metals if the articles to be plated are polarized anodically a minute or two before plating.²⁴ Sometimes it may be necessary to use auxiliary anodes or to shape the anode similarly to that of the surface to be plated.

Chromium anodes are not used commercially in chromium-plating solutions. Chromium has a tendency to dissolve too readily when used as anode, and it is more expensive to supply chromium as anodes than to use the acid. It is therefore more economical to supply the chromium ions by introducing the CrO₃ into the bath directly. Chromic acid must therefore be added periodically to maintain the chromium content. A hydrometer may be used as a basis for determining the chromium content; solution 9, above, has a specific gravity of about 1.18 (22.1° Bé.), but frequent chemical analyses of the solution for the chromic acid content, as well as for the acid radical content (SO₄), are very desirable. The content of CrO₃ should not be allowed to drop more than 10 per cent below its original concentration. Lead and sometimes steel anodes are used commercially, lead being preferred,^{20, 28} for it does not contaminate the bath. The anode area should be as large as possible.

During the plating operation hydrogen is evolved at the cathode and oxygen on the anode. This evolution of gas forms a fine spray of acid

²⁴ O. P. Watts, *Trans. Am. Electrochem. Soc.*, **52**, 177 (1927).

which if allowed to pass off into the room is harmful to the operators. Special ventilation is therefore important in chromium plating. Ventilating ducts should be placed directly along the upper edges of the tank.

Chromium plate, like practically all electroplated deposits, is porous, so that for outdoor use it is not the practice to deposit chromium directly on iron or steel, except on stainless steel. At some plants a non-porous intermediate layer is plated. If the article to be plated is a non-porous metal, nickel forms an ideal intermediate plate, owing to its relatively impervious deposit and its resistance to corrosion in the atmosphere. Also, nickel can be deposited to produce a fine-grained surface which can be highly colored (polished), thus serving as a desirable base for chromium, which will deposit in a layer requiring no further polishing. If the base metal is porous, the nickel plate too will be porous. Such base metals should be given a light deposit of nickel, followed by a heavy coat of very soft copper. The surface of the copper should be flowed (buffed) on a polishing wheel to close the pores. This should again be followed by a coat of nickel. This nickel is then highly colored and plated with chromium.

Chromium plating on nickel requires about 5 minutes or less for decorative articles, but the plating of the undercoating of nickel requires about 40 minutes.

Chromium plate on zinc is unsatisfactory, owing, as believed by some, to the zincification of the chromium. This also is true when chromium is plated on brass. If the deposit is thin, the chromium will disappear in a few months. If the chromium is thick, a dark-colored supposedly chromium-zinc alloy is formed between the zinc and the brass; this layer is non-adhesive and results in subsequent peeling off of the chromium. For first-class work, therefore, zinc and brass are given a coat of nickel.²⁷ Chromium can be successfully plated on aluminum.

Table XV, prepared by Griffiths,²⁸ shows the commercial procedure for producing chromium finishes.

Cobalt Plating. Cobalt plating is but little used, although there was a time when it appeared likely to gain considerable commercial importance. The failure is in part due to the fact that on account of other outlets for cobalt, particularly in steel and other alloys, its price has increased; it oxidizes more readily than nickel and chromium and is therefore not suitable for heating appliances; the introduction of chromium plating has further retarded its development.

²⁷ W. M. Phillips, *Trans. Electrochem. Soc.*, **59**, 379 (1931).

²⁸ W. T. Griffiths, *Electroplaters' and Depositors' Tech. Soc.*, June 17, 1931; *Metal Ind. (London)*, **39**, 444 (1931).

TABLE XV

COMMERCIAL ELECTROPLATING PROCEDURE

A—Grinding, polishing, or buffing.	G —Hand pumice scrub.
B—Wash with organic solvent.	H —Sulphuric acid dip.
C—Hot alkaline wash.	K —HF dip.
D—Alkaline electrolytic cleaning.	Cu—Acid copper plating.
E—Alkaline electrolytic cleaning containing sodium and copper cyanides.	Cy—Cyanide copper plating.
F—Muriatic acid dip.	Ni—Nickel plating.
	Cr—Chromium plating.

Plant	Base Metal	Coatings (In order applied)	Sequence of Operations
Bumpers, etc.	Mfg. Steel	Ni	A-D-F-Ni
	Mfg. Steel	Ni	A-B-D-F-E-Ni
	Steel	Ni-Cu-Ni-Cr	A-D-F-G-F-Ni-Cu-Ni-A-Cr
	Auto. Steel	Cy-Ni-Cr	A-D-F-Cy-A-C-H-Ni-A-C-Cr-A
	Auto. Steel	Ni-Cu-Ni	A-E-Ni-Cu-A-C-Ni-A
	Auto. Steel	Cy-Ni	A-Cy-A-C-Ni-A
Radiators, etc.	Steel	Cy-Cu-Ni-Cr	A-G-D-F-Cy-Cu-A-G-D-F-Ni-A-Cr
	Auto. Steel	Ni-Cu-Ni-Cr	A-D-F-Ni-Cu-A-Ni-A-Cr
	Auto. Steel	Cy-Ni-Cr	A-D-F-G-Cy-A-D-F-C-G-Ni-A-D-Cr
	Mfg. Steel	Cy-Ni	A-E-F-Ni-E-F-Ni
	Auto. Steel	Cy-Ni-Cr	A-C-D-E-Cy-Ni-A-D-H-Cr
	Auto. Steel	Cy-Ni-Cr	A-D-F-Cy-A-D-Cy-F-Ni-A-Cr
	Auto. Brass	Ni-Cr	A-D-C-F-Ni-A-D-Cr

Cobalt plate, however, has a pleasing appearance, somewhat like that of nickel, with a slightly bluish cast. It has an advantage over nickel in that much higher current densities can be used than in nickel plating. The work by Watts²⁹ on cobalt and nickel plating led to higher current densities in nickel plating in connection with the single salt solution, but not as high as for cobalt plating. Extensive work on cobalt plating was done by Kalmus and his associates,³⁰ and the bath composition given below is from their work.³¹

²⁹ O. P. Watts, *Trans. Am. Electrochem. Soc.*, **23**, 99 (1913).

³⁰ H. T. Kalmus, C. H. Harper, and W. L. Savell, Canada Dept. of Mines, *Ann. Rept.* 334 (1915); and *Trans. Am. Electrochem. Soc.*, **27**, 75 (1915).

³¹ Recalculated to grams per liter by Blum and Hogaboom. In the following pages all plating solution formulas unless otherwise stated are taken with permission from W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming*, second edition, McGraw-Hill Book Company, New York, 1930.

11. COBALT PLATING SOLUTION.

	g./l.	oz./gal.
Cobalt sulphate, CoSO_4	278	37.0
Or $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	504	68.0
Sodium chloride, NaCl	17	2.3
Boric acid, H_3BO_3 , about	45	6.0

Temperature, room

Current density 3.5 to 17.5 amp. per sq. dm. (33 to 163 amp. per sq. ft.).

Both cast and rolled anodes, containing 96 to 98 per cent cobalt, have proved successful.

Gold Plating. Gold plating is used for producing a decorative or a protective coating on various articles. Gold is not appreciably attacked by any single acid and is indeed attacked by very few reagents, which makes it valuable as a protective coating for the linings of calorimeter bombs and on analytical weights. Gold, being low in the electromotive series, has no electrochemical protection on baser metals; in fact, like tin on iron, it accelerates corrosion if any of the base metal is exposed.

Gold plating may be done by three different methods, each finding commercial application for certain classes of work. These methods are: (a) electroplating; (b) salt-water plating; and (c) dip plating.

(a) *Electro Gold Plating.* The gold content is supplied by gold chloride, by one of the double alkali cyanides of gold, or by gold fulminate. Practically always the gold compound used is made from gold chloride, AuCl_3 , which is purchased as chloroauric acid, $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ or $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$. The sodium or potassium gold cyanide is produced by treating gold chloride with the alkali cyanide:



forming the double aurous cyanide, in which the gold has a valence of 1 instead of 3 as in the chloride. The electrochemical equivalent of the gold in the cyanide is therefore three times as great as in the chloride. The fulminate, a highly explosive compound of gold when dry, is prepared by treating gold chloride with ammonium hydroxide, NH_4OH , obtaining the fulminate, $\text{Au}(\text{NH}_3)_2(\text{OH})_3$, as a precipitate. When one of the alkali cyanides is added to the fulminate, however, the double aurous cyanide, $\text{NaAu}(\text{CN})_2$, is produced with liberation of ammonia. Gold-plating solutions may be made by a method known as the "porous cup" method. An iron or other insoluble cathode is placed in a porous cup which contains a nearly saturated solution of sodium cyanide. Out-

side the cup is placed a solution of sodium cyanide containing about 19 g. per liter ($2\frac{1}{2}$ oz. per gal.). An anode of pure gold is placed in the outer solution, and a current is passed through the cell until the proper amount of gold has dissolved, which is determined by weighing the anode. Anodes of gold alloys for producing plating solutions for green gold, white gold, or red gold may also be used.

The following gold plating solutions are in use.

12. GOLD PLATING SOLUTION.

	g./l.
Metallic gold (as fulminate or cyanide)	2.1 5.0 dwt./gal.
Potassium cyanide, KCN.....	15.0 2.0 oz./gal.
Sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.	4.0 0.5 oz./gal.

13. GOLD PLATING SOLUTION.

	g./l.
Metallic gold (as fulminate or cyanide)	4.2 10.0 dwt./gal.
Potassium cyanide, KCN.....	15.0 2.0 oz./gal.

14. GOLD PLATING SOLUTION.³²

	g./l.	oz./gal.
Sodium gold cyanide, $\text{NaAu}(\text{CN})_2$	5.6	0.75
Sodium cyanide, NaCN.....	45.0	6.0

Temperature for above baths 60 to 82° C. (140 to 180° F.).

Current density 0.1 to 1.0 amp. per sq. dm. (1.0 to 10 amp. per sq. ft.).

If gold anodes are used, the gold content of the solution tends to increase, so that sometimes anodes may be of nichrome, graphite, or duriron.³³ When duriron is used in cyanide solutions there may be formation of ferrocyanides, so that nichrome is to be preferred for anodes.³⁴

Green gold plating solutions may be prepared by adding the proper amount of double silver cyanide to a regular gold-plating solution, so that the desired tint is produced. Platinum anodes, or anodes of gold and silver, may be used. A typical formula for green gold solution is:

15. GREEN GOLD PLATING SOLUTION.

	g./l.
Metallic gold (as chloride).....	2.1 5 dwt./gal.
Metallic silver (as chloride).....	0.1 0.25 dwt./gal.
Sodium cyanide.....	30.0 4 oz./gal.

³² J. E. Underwood, *Metal Cleaning and Finishing*, 1, 514 (1929).

³³ M. deKay Thompson, *Trans. Am. Electrochem. Soc.*, 54, 323 (1928).

³⁴ G. B. Hogaboom, *ibid.*, 54, 327 (1928).

(b) *Salt-Water Gold Plating.* In salt-water plating, no external current is needed. The plating cell is a voltaic cell with a sheet of zinc as an anode dipping into a strong solution of salt, NaCl. The article to be plated serves as cathode and dips into the gold-plating solution. The salt-water anolyte and the gold solution catholyte are separated by a porous diaphragm. Generally this diaphragm is a porous cup containing the plating solution. The cup is set in a larger copper can containing the salt water; and placed around the porous cup, but not touching it, is the sheet of zinc bent in cylindrical form. This sheet extends above the tops of the porous cup and the copper can; the cathode bar, from which the article to be plated is suspended, rests on the top of the zinc sheet; this completes the external circuit of the cell.

A typical salt-water gold-plating solution is as follows:

16. GOLD SALT-WATER SOLUTION.

	g./l.	
Gold (as fulminate).....	1.2	3.0 dwt./gal.
Sodium ferrocyanide, Na ₄ Fe(CN) ₆ ·10H ₂ O.....	15.	2.0 oz./gal.
Sodium phosphate, Na ₂ HPO ₄ ·12H ₂ O.....	7.5	1.0 oz./gal.
Sodium carbonate, Na ₂ CO ₃	4.0	0.5 oz./gal.
Sodium sulphite, Na ₂ SO ₃	0.15	0.02 oz./gal.

Salt-water gold plating is used where relatively thin coatings of gold are satisfactory. The cost of plating by this method is less than when the regular gold solution is used, but the plate will not stand as hard wear.

(c) *Dip Gold Plating.* This is a process in which the gold is plated by "deposition by immersion," also called "by replacement," conditions encountered frequently as in copper, tin, mercury, and silver plating. The method is employed on low-priced articles where but a thin "wash" of gold is sufficient, the thickness being as low as 0.000025 mm. (0.000001 in.). The deposit, however, is quite dense and adheres well to the base metal, for the electrochemical equivalent of gold is high compared to that of the base metal. When gold is plated on brass by this method, the reaction may be represented by



It will be seen from this that the weight of gold deposited is about six times that of the zinc dissolved, the volume being about twice that of the zinc dissolved, so that a dense deposit of gold is formed.

Good deposits of gold by immersion are obtained only on copper or brass, but deposits may be obtained on any metal above gold in the electromotive series, which includes practically all metals. Articles

other than brass or copper should be plated with copper or bronze before dip gold plating.

17. GOLD DIP SOLUTION.

	g./l.
Gold (as fulminate).....	2.1 5 dwt./gal.
Sodium carbonate, Na_2CO_3	45.0 6 oz./gal.
Sodium cyanide, NaCN	30.0 4 oz./gal.

Temperature, 80° C. (176° F.)

The solution should be boiled for several hours in a stone crock or enameled kettle before use.

Iron Plating. With the large tonnage of iron and steel used annually, it might be expected that the electrodeposition of iron would be of considerable importance. This, however, is not true, although the electrodeposition dates back to 1860. This is because a large proportion of all electroplating is for the purpose of ornamentation or protection of baser metals against corrosion. It is evident that for both these purposes electrodeposited iron would find little application. For electrotypes on which a wear-resistant surface is necessary, copper has been replaced by nickel, and it was once expected that iron might replace nickel for electrotypes which would be subjected to great wear, but chromium is proving very excellent for this purpose.

Electrodeposited iron has some application, however, especially in the refining of iron. The Western Electric Company at Hawthorne, Illinois, once had a schedule of 25,000 lb. electrolytic iron weekly for the production of transformer cores, but this method is no longer used.³⁵ Electroplating of iron is also used for building up iron parts that have become worn or have been improperly machined. On occasions much money has been saved by electrodepositing iron, but nickel is also very satisfactory for replacing worn parts.³⁶

In France a process has been developed for the production of tubing³⁷ which, after the hydrogen is removed by heating, is ductile and can be easily welded, and readily drawn or spun. In connection with the recent advances in powder metallurgy, a process has been developed at the Mellon Institute for Industrial Research for the production of electrolytic iron powder.³⁸ Studies are being conducted on the electroforming of

³⁵ S. Skowronski, *Trans. Am. Electrochem. Soc.*, **45**, 358-59 (1924).

³⁶ W. E. Hughes, *Electrician*, **87**, 640 (1921); *Trans. Am. Electrochem. Soc.*, **41**, 317 (1922); *Chem. Met. Eng.*, **26**, 267 (1922).

³⁷ Boucher, French Patent 458,294 (1912), U. S. Patent 1,086,132 (1914).

³⁸ Anon., *Ind. Eng. Chem., News Ed.*, **18**, 291 (1940).

molds for rubber, glass, and plastics.³⁹ A summary on the electrodeposition of iron was published by Thomas in 1942.⁴⁰

One of the difficulties encountered in iron-plating baths is that the ferrous (Fe^{++}) salts tend to oxidize to ferric (Fe^{+++}) with the precipitation of basic salts. This can be avoided by keeping the solution acid, but, since iron is above hydrogen in the electromotive series, considerable hydrogen will plate out unless the ratio of Fe^{++} to H^+ is high. The acidity, therefore, requires careful and frequent regulation.

Electrodeposition of iron has a tendency to form cracked, spongy, or pitted deposits, but it has been shown by McFayden,⁴¹ Hughes,⁴² and Alley⁴³ that iron can be deposited free from slag inclusions and pinholes, with no tendency to pitting or corrosion.

In practically all iron baths the iron ions are supplied by ferrous sulphate or chloride or by both. The original Fisher-Langbein solution appears to give as good results as any other solution thus far developed. The patent calls for 450 g. ferrous chloride, aq.; 500 g. calcium chloride; and 750 cc. water. Calculated to grams per liter, this corresponds to:

18. IRON CHLORIDE SOLUTION.

	g./l.	oz./gal.
Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	300	40
Calcium chloride, CaCl_2	335	45

Temperature, 90° C. (194° F.).

Current density up to 20 amp. per sq. dm. (186 amp. per sq. ft.).

19. IRON SULPHATE SOLUTION.⁴⁴

	g./l.	oz./gal.
Ferrous ammonium sulphate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	350	47
Sulphuric acid, H_2SO_4 , about.....	0.25	0.03

Temperature about 18° C. (65° F.).

Current density about 2 amp. per sq. dm. (19 amp. per sq. ft.).

Anodes for iron plating may be of carbon, graphite, wrought iron, or low-carbon steel.

³⁹ Bull, Bishop, Orbaugh, and Wallace, *Metal Ind. (New York)*, **37**, 461 (1939).

⁴⁰ C. T. Thomas in *Modern Electroplating*, pp. 213, 214, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 499-506 (1942).

⁴¹ W. A. McFayden, *Trans. Faraday Soc.*, **15**, 98 (1920).

⁴² W. E. Hughes, Dept. Sci. & Ind. Research, London, *Bull.* **6**, 1922.

⁴³ J. D. Alley, *Machinery*, **30**, 202 (1923); *Brass World*, **19**, 373 (1923).

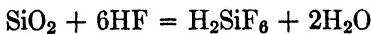
⁴⁴ W. A. McFayden, *Trans. Faraday Soc.*, **15**, 98 (1920).

Addition agents have been studied by Watts and Li⁴⁵ and by Hineline.⁴⁶ Chromous chloride, CrCl₂, is among the most satisfactory addition agents. Other substances used are hydroquinone and sulphur dioxide.

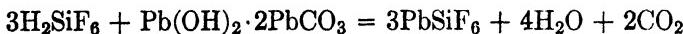
Lead Plating. The electrodeposition of lead has not found wide industrial application. Although lead cannot, like tin, be applied directly to steel by hot dipping, for the adhesion of the lead to the steel is poor, it can be thus applied if about 10 to 20 per cent tin is added to the lead. This is the "terneplate" used for roofings.

Although lead can be deposited from a variety of solutions, the only ones that have found commercial application are the fluosilicate, fluoroborate, and perchlorate solutions. The fluosilicate and fluoroborate solutions were developed to commercial importance by Betts.⁴⁷

Fluosilicic acid, H₂SiF₆, can be prepared by treating pure sand or quartz, SiO₂, with hydrofluoric acid, HF:



This is treated with commercial white lead:



An excess of fluosilicic acid is desirable, for it increases the conductivity of the solution and decreases the lead-ion concentration.

The fluosilicate bath recommended by Betts contains 8 per cent lead and 15 to 16 per cent SiF₆, which corresponds to about the following composition:

20. LEAD FLUOSILICATE SOLUTION.

	g./l.	oz./gal.
Lead, as PbSiF ₆	80	10.75
Fluosilicic acid, H ₂ SiF ₆	150	20
Glue.....	0.2	0.025

Temperature, 35 to 40° C. (95 to 105° F.).

Current density, 0.54 to 8.6 amp. per sq. dm. (5 to 80 amp. per sq. ft.).

The Betts process was first used for lead refining only, and was one of the first solutions to be successful commercially. It is used as a refining bath by the U. S. Lead Refining Company, East Chicago, Illinois; the Consolidated Mining and Smelting Company, Trail, British Columbia; and the American Smelting and Refining Company, Omaha, Nebraska.

⁴⁵ O. P. Watts and M. H. Li, *Trans. Am. Electrochem. Soc.*, **25**, 529 (1914).

⁴⁶ H. D. Hineline, *ibid.*, **48**, 119 (1923).

⁴⁷ A. G. Betts, *Lead Refining by Electrolysis*, John Wiley & Sons, New York, 1908.

A bath used by Reeve⁴⁸ is made up as stated below. It was used as received from a refinery and is given in percentage composition. The following formula would probably reproduce it closely:

21. LEAD FLUOSILICATE BATH.

	g./l.	oz./gal.
Lead, as PbSiF ₆	180	24
Fluosilicic acid, H ₂ SiF ₆	29	3.9
Glue.....	4	0.53

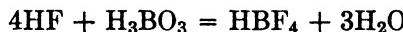
Temperature, 35 to 38° C. (95 to 100° F.).

Current density, 5 amp. per sq. dm. (46.5 amp. per sq. ft.).

The above solution was used by Reeve for plating the interior of gas shells.

It is not easy to prepare a small amount of fluosilicic acid, and for small-scale work it is advisable to purchase the complete plating solution from a lead refinery.

The fluoborate solution is another important solution for lead plating. It is prepared by dissolving boric acid crystals, H₃BO₃, in hydrofluoric acid, HF, the process being carried out in a lead-lined or hard-rubber tank. For the sake of simplicity the reaction may be represented by:



After the solution has cooled, white lead is added in the form of a tin paste with water, forming lead fluoborate, Pb(BF₄)₂. The precipitate of lead sulphate is allowed to settle, and the clear solution is transferred to the plating tank.

22. LEAD FLUOBORATE BATH.⁴⁹

	g./l.	oz./gal.
Basic lead carbonate, white lead, Pb(OH) ₂ ·2PbCO ₃	150	20
Hydrofluoric acid, HF (the 50% com- mercial acid).....	240	32
Boric acid, H ₃ BO ₃	105	14
Glue.....	0.2	0.025

Temperature, 25 to 40° C. (77 to 105° F.)

Current density 1 to 2 amp. per sq. dm. (9.3 to 19 amp. per sq. ft.).

With mechanical agitation the current density can be almost doubled.

⁴⁸ A. G. Reeve, *Trans. Am. Electrochem. Soc.*, **35**, 389 (1919).

⁴⁹ W. Blum, F. J. Liscomb, Z. Jencks, and W. E. Bailey, *ibid.*, **36**, 260 (1919).

Lead fluoborate like the fluosilicate solution is difficult to prepare in the plating shop. Concentrated solutions can be purchased which require only the addition of water to prepare them for the plating tank; glue, if desired, is also added at the shop. Such a solution⁵⁰ consists of:

	g./l.	oz./gal.
Lead fluoborate, $\text{Pb}(\text{BF}_4)_2$	677	90.5
Free fluoboric acid, HBF_4	80	10.7
Free boric acid, H_3BO_3	5%	5%

Another type of lead-plating solution is the perchlorate solution.⁵¹ This is not widely used, partly because the perchloric acid, HClO_4 , is relatively expensive and partly because of a probably unwarranted fear of explosions.

23. LEAD PERCHLORATE BATH.

	g./l.	oz./gal.
Lead, as basic lead carbonate.....	60	8
Perchloric acid, HClO_4	40	5.3
Oil of cloves, or peptone.....	4	0.5

Temperature, about 18° C. (65° F.).

Current density, 2 to 3 amp. per sq. dm. (19 to 27 amp. per sq. ft.).

Lead anodes used for all lead plating should contain preferably 97.5 per cent lead, or more.

Mechanical agitation is desirable in lead plating; owing to the readily oxidizable properties of lead, air agitation does not yield satisfactory results.

The protective action of lead on steel is improved if the steel is first given a "strike" of copper. In fluosilicic baths the necessity of copper plating can be avoided by dipping the steel in a solution of glue, prior to plating.

Nickel Plating. Nickel plating is one of the most important electroplating industries. Nickel is used primarily as a protective coat on steel, brass, and zinc die castings. It is commonly covered with a coating of chromium plate. Nickel is used to some extent to repair worn parts and for electroforming printing plates, phonograph masters, sheet, tube and screen.

The nickel content of nickel-plating baths is furnished by nickel sulphate, either as the single salt $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, or as the double salt, nickel

⁵⁰ General Chemical Company, Pittsburgh, Pennsylvania.

⁵¹ F. C. Mathers, *Trans. Am. Electrochem. Soc.*, **17**, 261 (1910); **23**, 153 (1913).

ammonium sulphate, $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Nickel ions may also be supplied by nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and by basic nickel carbonate, $\text{NiCO}_3 \cdot \text{Ni}(\text{OH})_2$; but in addition to furnishing nickel ions, the former serves as a convenient means of supplying chloride ions helpful in increasing anode corrosion, the latter as a means of neutralizing the solution, both accomplishing their objects without adding foreign cations. Zinc, copper, and iron may be contained in the nickel salts as impurities.⁵² Zinc should be present in quantities under 0.05 per cent; copper, under 0.03 per cent. The following specifications for allowable impurities in nickel-plating solutions have been proposed:

	MAXIMUM PER CENT
Zinc	0.05
Copper	0.02
Iron	0.08
Free Acid	0.10
Insoluble	0.10

By neutralizing the nickel solution with ammonia or nickel carbonate to $p\text{H} = 6.7$, and then filtering, the zinc and copper may be removed almost completely. Iron is not harmful up to 0.1 per cent; in fact, some of the nickel anodes formerly in commercial use contained 6 per cent iron, the iron being added purposely to promote greater anode corrosion. Because nickel solutions are operated at nearly neutral conditions, the iron held in solution is limited automatically to an amount that is not harmful.

As is true of most heavy metal sulphates, the conductivity of a nickel sulphate solution is low; therefore other salts are added to increase it. Ammonium, potassium, sodium, and sometimes magnesium sulphates are added for this purpose. Chlorides will also materially increase the conductance of nickel-plating solutions, and in addition they help to increase anode corrosion.

The sulphates added to the nickel solution also decrease the dissociation of the nickel sulphate owing to the common-ion effect. Cyanide nickel solutions, like cyanide copper solutions, are possible, but are little used commercially because the anode corrosion in such solutions is poor. Some nickel-plating-solution formulas for plating on zinc call for citrates and tartrates, which prevent the deposition of nickel by immersion, their action probably being due to a decrease in the dissociation of the nickel sulphate by the formation of complex ions.

⁵² M. R. Thompson and C. T. Thomas, *ibid.*, 42, 79 (1922).

Lead fluoborate like the fluosilicate solution is difficult to prepare in the plating shop. Concentrated solutions can be purchased which require only the addition of water to prepare them for the plating tank; glue, if desired, is also added at the shop. Such a solution⁵⁰ consists of:

	g./l.	oz./gal.
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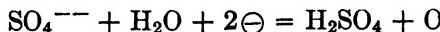
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⁵² M. R. Thompson and C. T. Thomas, *ibid.*, 42, 79 (1922).

Pure nickel anodes become "passive" in nickel sulphate solutions; that is, the nickel does not go into solution in accordance with Faraday's law. Instead of all the current entering the cell according to the reaction



some enters the cell according to the reaction



oxygen is liberated, and the solution becomes acid. Ammonium sulphate and ammonium chloride and nickel, magnesium, and sodium chlorides and fluorides⁵³ are added to increase the anode corrosion. The addition of iron and carbon to the nickel anodes is considered helpful in anode corrosion. Formerly an iron content above 5 per cent was considered desirable, but, owing to improvements in the bath compositions such as the addition of chlorides, the iron content of the anodes is kept at a minimum.

Nickel is above hydrogen in the electromotive series, and therefore, in contrast to copper which is below hydrogen, it cannot be plated from a decidedly acid solution. If the pH is below 4 (high acidity), the deposit will crack and pit; if the pH is above 6.5, the deposits will be dark and will be likely to crack and curl.⁵⁴ A high acidity will cause a decreased cathode efficiency owing to liberation of hydrogen in place of some of the nickel; a noticeable gassing at the cathode is therefore a warning that the solution is becoming too acid. A solution that has become too acidic may be neutralized by the addition of basic nickel carbonate, $\text{NiCO}_3 \cdot \text{Ni(OH)}_2$. A convenient preventive for overacidity is a buffer, i.e., a compound that resists to a considerable degree the action of both acids and bases, thus holding the solution at a fairly constant pH value.⁵⁵ Weak acids (i.e., those with a low degree of ionization), such as boric, citric, tartaric, and acetic, all of which are finding use in nickel-plating solutions, serve as buffers to regulate the acidity; of these, boric acid, H_3BO_3 , is used most commonly.

Nickel anodes have been discussed to some extent above, under passivity. Formerly cast-nickel anodes containing about 90 per cent nickel and 5 per cent iron were common, the iron together with some carbon being added to reduce passivity; but now, because of improvement in the solution composition, 99 per cent nickel anodes are to be preferred. More recently so-called depolarized anodes containing nickel oxide have

⁵³ W. Blum, *ibid.*, **39**, 459 (1921); E. G. Lovering, *Monthly Rev., Am. Electroplaters' Soc.*, **8**, 3 (1921).

⁵⁴ M. deKay Thompson, *Trans. Am. Electrochem. Soc.*, **41**, 333 (1922).

⁵⁵ Buffer solutions are discussed by Creighton in Vol. I.

come into use. Anodes may be cast or rolled, the rolled ones corroding more uniformly when properly annealed.

In operating the plating bath the temperature is generally that of the room, unless the composition is especially modified to permit higher temperatures. The solution should be slightly acid, not neutral, the pH being preferably between 5 and 6. Excessive acidity causes gassing and pitting at the cathode and lowered cathode efficiency. Commercial nickel-plating procedure is shown in Table XV, page 128.

In plating nickel on zinc and aluminum, the nickel may be deposited by immersion, because zinc and aluminum are above nickel in the electromotive series. Such deposits are dark and adhere poorly. Good deposits can be obtained by using an initially high current density or by reducing the nickel-ion concentration. Sodium citrate reduces the deposition of nickel by immersion, because of the reduced ionization of the nickel. Nickel plate on zinc has the same disadvantage that tin plate has on iron; if any of the base metal, being higher in the electromotive series than the metal plating it, is exposed, it will corrode faster than if the plating metal were not present.

Black nickel plating may be applied to copper, brass, and zinc;⁵⁵ if iron is to be plated it must first be plated with copper or zinc. The current density is low, 0.1 to 0.2 amp. per sq. dm. (0.9 to 1.9 amp. per sq. ft.). Black nickel plating is used for hardware, especially that for military service where bright nickel would be undesirable.

It is difficult to plate over old nickel plate; if any old work requires replating the old nickel should be stripped. Nickel may be stripped from brass by making the nickel-plated piece the anode in a dilute hydrochloric acid solution (1 : 20); for stripping from steel a concentrated solution of sulphuric acid should be used. In either case the cathode may be a sheet of lead. Nickel may also be stripped from steel by treating with a concentrated solution of nitric acid without electrolysis; the acid attacks the iron only slightly.

24. NICKEL DOUBLE SALT SOLUTION.

	g./l.	oz./gal.
Nickel ammonium sulphate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	105	14
Ammonium chloride, NH_4Cl	15	2
Boric acid, H_3BO_3	15	2

Temperature, 20 to 30° C. (68 to 86° F.).

Current density, 0.3 to 0.6 amp. per sq. dm. (3 to 6 amp. per sq. ft.).

⁵⁵ W. Blum, *Trans. Am. Electrochem. Soc.*, **34**, 169 (1918); G. B. Hogaboom, T. F. Slattery, and L. B. Ham, *Natl. Bur. Standards Tech. Paper* 190, 1921; J. Haas, Jr., *Metal Ind. (New York)*, **19**, 23, 73 (1921).

25. NICKEL SINGLE SALT SOLUTION.

	g./l.	oz./gal.
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	105	14
Ammonium chloride, NH_4Cl	15	2
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	15	2
Boric acid, H_3BO_4	15	2

Temperature, 20 to 30° C. (68 to 86° F.).

Current density, 0.5 to 2 amp. per sq. dm. (5 to 19 amp. per sq. ft.).

In 1916 Watts⁵⁷ introduced a bath for high-speed plating, which with some modifications is now widely used as the well-known bright nickel bath, also called a high-speed bath. The solution is used above room temperature.

26. NICKEL SOLUTION, MODIFIED WATTS SOLUTION.⁵⁸

	g./l.	oz./gal.
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	240	32
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	45	6
Boric acid, H_3BO_4	30	4

Temperature, 50 to 60° C. (122 to 140° F.).

Current density, 2 to 5 amp. per sq. dm. (19 to 47 amp. per sq. ft.).

The pH of the solution should be 1.5 to 3.0 or 4.5 to 5.6.

27. NICKEL SOLUTION FOR PLATING ON ZINC.⁵⁹

	g./l.	oz./gal.
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	70	9
Ammonium chloride, NH_4Cl	15	2
Sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	160	22
Or		
Na_2SO_4	71	9
Boric acid, H_3BO_4	15	2

Temperature, 20 to 30° C. (68 to 86° F.).

Initial current density, 1.5 to 3 amp. per sq. dm. (14 to 27 amp. per sq. ft.).

⁵⁷ O. P. Watts, *Trans. Am. Electrochem. Soc.*, **29**, 395 (1916).

⁵⁸ W. L. Pinner, G. Soderberg, and E. M. Baker, in *Modern Electroplating*, p. 238, The Electrochemical Society, Columbia University, New York, 1942.

⁵⁹ M. R. Thompson, *Trans. Am. Electrochem. Soc.*, **47**, 163 (1925).

Platinum Plating. Electroplating of platinum has had very limited application in the past but may have considerable applications. A solution in use is:

28. PLATINUM CHLORIDE SOLUTION.

	g./l.
Platinum (as chloride).....	5 12 dwt./gal.
Ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$..	45 6 oz./gal.
Sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. .	240 32 oz./gal.

Temperature, 70° C. (158° F.).

Current density 0.1 amp. per sq. dm. (1 amp. per sq. ft.) or less.

Each salt is dissolved separately in water, and the first two listed are poured together, after which the third is added. The mixture is then boiled until no odor of ammonia can be detected, which may take several hours.

Thin deposits of platinum give little protection from acid or fumes, and it is difficult to obtain thick, impervious layers.

A more recently developed solution ⁶⁰ is made up as follows:

29. PLATINUM DIAMMINONITRITE SOLUTION.

	g./l.
Platinum, as diamminonitrite,	
$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$	10 24 dwt./gal.
Ammonium nitrate, NH_4NO_3	100 13 oz./gal.
Sodium nitrite, NaNO_2	10 1.3 oz./gal.

Temperature, 90 to 95° C. (194 to 203° F.).

Potential, 4.5 volts.

The ingredients are dissolved not in pure water, but in distilled water containing about 5 per cent concentrated aqueous ammonium hydroxide, NH_4OH , by volume. The bath gives brilliant flashes in a few seconds.

Rhodium Plating.⁶¹ Rhodium is the only metal of the platinum group that is electroplated commercially on an extensive scale. The metal can be plated as bright deposits that require no buffing. The deposits are characterized by their high reflectivity, namely, 78 per cent, and are finding application for reflectors for searchlights and for motion-picture projectors. Rhodium is used as a thin deposit on silver-plated ware to

⁶⁰ W. Keitel, and H. E. Zschiegner, *Trans. Electrochem. Soc.*, **59**, 273 (1931).

⁶¹ K. Schumpelt, in *Modern Electroplating*, pp. 280-283, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 494-497 (1942).

prevent tarnishing in the salesroom. The hardness of the plate ranges between that of nickel and chromium. Rhodium is usually plated on an undercoat of nickel; this is particularly important when plating on zinc, tin, and lead alloys. It can be plated directly on silver, gold alloys, and platinum bases.

30. RHODIUM SULPHATE SOLUTION.

Sulphuric acid, H_2SO_4 ,			
C.P. concentrated.....	20 cc./l.	2.523 liquid oz./gal.	
Rhodium metal in prepared concentrated solution. ⁶² ...	2 g./l.	5 dwt./gal.	

31. RHODIUM PHOSPHATE SOLUTION.

Orthophosphoric acid, H_2PO_4 , 85%.....	40 cc./l.	5 to 6 liquid oz./gal.	
Rhodium metal in prepared concentrated solution. ⁶² ...	2 g./l.	5 dwt./gal.	

In making up either bath it is important to add the acid to the water before adding the rhodium solution, to prevent partial precipitation of rhodium compound by hydrolysis.

When making plating solutions containing high-priced precious metals, a compromise must be adopted regarding the metal concentration. It should not be too high in order to keep the initial investment and the dragout losses low; on the other hand the solution should contain enough metal for quick coverage and a reasonable cathode efficiency.

Silver Plating. Silver plating has for many years found application for ornamental purposes and where "sterling" would be too expensive. It is used on tableware such as knives, forks, spoons, trays, and casserole holders; headlight reflectors; musical and surgical instruments; chemical-engineering equipment; electric-circuit parts; and to a much more limited extent on automobile and casket hardware and electric fixtures. It is a white metal, taking a high polish with a pleasing luster. Its power to reflect light for ordinary wavelengths exceeds that of practically all other metals. It is chemically quite stable; it is not oxidized on exposure to air, but is readily tarnished by sulphides, even when present in the air in but traces, as hydrogen sulphide obtained from the combustion of coal or gas. The sulphides present in such foods as eggs and mustard also

⁶² It is difficult to prepare a suitable rhodium salt in a constant and uniform solution; this is best done during the manufacture of the salt under rigorous scientific control. The metal, therefore, for plating purposes is sold in the form of a concentrated compound in solution and can be obtained as such from Baker and Company, Inc., Newark, N. J.

tarnish silver. The surface of silver used only for ornamental purposes can be protected by a coat of lacquer, but for tableware this is obviously impracticable. The tarnish of silver sulphide can be removed without loss of silver by heating the silverware in a dilute solution of sodium bicarbonate, NaHCO_3 , and sodium chloride (table salt), NaCl (a tea-spoon full of each per quart of water is sufficient). The silver must be in contact with a sheet of zinc or aluminum, in fact, an aluminum kettle will serve well as a container and as anode. A local couple is thus produced, the aluminum or zinc acting as anode and going into solution, and hydrogen plating out on the silver cathode and reducing the silver sulphide to metallic silver.

By referring to Table VII, page 38, it will be noted that silver is near the lower end of the electromotive series. Difficulty is therefore experienced in plating silver on metals above it in the series, for silver deposits by contact, forming a poorly adhering deposit. This is largely a matter of electrode potentials; it was studied by Frary and Porter,⁶³ who found that the potential of silver can be made more negative by having free cyanide present. In fact, all commercial silver-plating solutions are cyanide solutions with considerable free cyanide.⁶⁴ In the silver coulometer, however, a silver nitrate, AgNO_3 , solution is used because the current efficiency is 100 per cent, and the nature of the deposit is of secondary importance.

The cyanide reduces the silver-ion concentration, but, even with the low ion concentration of the plating baths, silver will deposit by contact. For plating on iron and steel, therefore, it is customary first to plate the article for a few seconds in a very dilute "strike" which contains a small amount of silver, some copper, and much free cyanide. This plating is followed by plating in a second strike containing a little more silver and also free cyanide,⁶⁵ after which plating is continued from the regular plating solution. Copper, brass, and alloys of tin are first coated with mercury by immersion in a solution of mercuric chloride, HgCl_2 , which is called the "blue dip," or by immersion in a mercuric cyanide solution, $\text{Hg}(\text{CN})_2$. They are then given a strike and are plated in the regular solution. Nickel alloys require no mercury dip.

The silver ions of a silver-plating solution are furnished by the double silver cyanides, $\text{NaAg}(\text{CN})_2$ or $\text{KAg}(\text{CN})_2$. These double cyanides are the result of adding the silver and alkali cyanides separately:



⁶³ F. C. Frary and R. E. Porter, *Trans. Am. Electrochem. Soc.*, **28**, 307 (1915).

⁶⁴ For a study of silver deposition from sulphate, nitrate, fluoborate, and fluoride solutions, see E. B. Sanigar, *Trans. Electrochem. Soc.*, **59**, 307 (1931).

⁶⁵ R. Namias, *J. Soc. Chem. Ind.*, **23**, 754 (1904).

The double cyanide dissociates:



This ionization produces no silver ions, but the complex cyanide ion further ionizes to a small extent:



There is thus produced a favorable condition for electroplating: the metal-ion concentration is low, but there is, so to speak, an inexhaustible reserve supply to replace the few silver ions as fast as they are removed. This low silver-ion concentration due to the excess cyanide also has the effect of placing silver farther up the scale in the electromotive series, so that it is possible to plate silver with very little hydrogen liberation, and with an efficiency very close to 100 per cent. This is not true of copper cyanide solutions, from which hydrogen plates out at a lower potential.⁶⁶ The cyanide also increases the conductivity of the solution and aids in the anode corrosion.

Although silver plating has been practiced for many years, no radical changes have been developed in the bath compositions or operating conditions. These are summarized by Barclay⁶⁷ as follows:

1. The desirable silver content of the solution is about 22 to 25 g. per liter (3 troy oz. per gal.).
2. The free cyanide should be equal to the combined cyanide, i.e., there should be 100 per cent free cyanide.
3. The presence of compounds such as hydroxide, carbonate, chloride, and cyanate (KCNO) is advantageous.
4. The current density should vary with the metal and free cyanide content, a current density of 0.3 to 0.33 amp. per sq. dm. (2.75 to 3.0 amp. per sq. ft.) being recommended, but densities above 0.9 amp. per sq. dm. (8 amp. per sq. ft.) have been employed successfully. The American practice is to use 0.43 to 0.54 amp. per sq. dm. (4 to 5 amp. per sq. ft.), and in bright baths from 0.67 to 0.86 amp. per sq. dm. (6 to 8 amp. per sq. ft.).
5. The temperature should range from 17 to 23° C. (63 to 73° F.).
6. Cyanide should be added at regular intervals to maintain the free cyanide content.
7. Baths give better results when used regularly than when used intermittently.

⁶⁶ O. P. Watts and A. Brann, *Trans. Am. Electrochem. Soc.*, **31**, 303 (1917).

⁶⁷ W. R. Barclay, *Trans. Faraday Soc.*, **18**, 515 (1921). This is part of a symposium on silver plating, including articles by G. B. Brook and L. W. Holmes, *ibid.*, **16**, 524, 538; F. Mason, *ibid.*, **16**, 534. See also F. C. Meale, *Monthly Rev., Am. Electroplaters' Soc.*, **4**, No. 9, p. 10 (1917).

The following are typical of baths in American silver-plating practice.

32. SILVER FIRST STRIKE FOR STEEL.

			g./l.
Metallic silver, Ag.....	0.01 N	1.2	3 dwt./gal.
As silver cyanide, AgCN...	0.01 N	1.5	0.2 troy oz./gal.
Copper carbonate,			
$\text{Cu}(\text{OH}_2) \cdot \text{CuCO}_3$	0.13 N	15.0	2.0 oz./gal.
Potassium cyanide, KCN..	1.0 N	68	9 oz./gal.

33. SILVER SECOND STRIKE FOR STEEL OR FIRST STRIKE FOR BRASS, NICKEL SILVER, AND BRITANNIA.

			g./l.
Metallic silver, Ag.....	0.05 N	5.0	12 dwt./gal.
As silver cyanide, AgCN...	0.05 N	6.5	0.8 troy oz./gal.
Potassium cyanide, KCN..	1.0 N	68	9 oz./gal.

A silver strike solution is always used at room temperature.

34. SILVER-PLATING SOLUTION, WHITE DEPOSITS.

			g./l.
Metallic silver, Ag.....	0.27 N	29	3.5 troy oz./gal.
As silver cyanide, AgCN...	0.27 N	35	4.4 troy oz./gal.
Total potassium cyanide,			
KCN.....	0.57 N	37	5.0 oz./gal.
Therefore free potassium cy-			
anide, KCN.....	0.30 N	19	2.5 oz./gal.
Potassium carbonate,			
K_2CO_3	0.55 N	38	5.0 oz./gal

35. SILVER-PLATING SOLUTION, BRIGHT DEPOSITS.

			g./l.
Metallic silver, Ag.....	0.27 N	29	3.5 troy oz./gal.
As silver chloride, AgCl....	0.27 N	39	4.7 troy oz./gal.
Total potassium cyanide,			
KCN.....	1.07 N	70	9.3 oz./gal.
Therefore free potassium cy-			
anide, KCN.....	0.53 N	34	4.5 oz./gal.
Potassium carbonate,			
K_2CO_3	0.55 N	38	5.0 oz./gal.
Temperature of the above two solutions, 24 to 32° C. (75 to 90° F.).			
Current density, 0.5 to 1.0 amp. per sq. dm. (5 to 10 amp. per sq. ft.).			

Increasing the current density improves the throwing power, anode and cathode polarization, and up to a certain extent improves the

appearance of the deposit.⁶⁸ However, the recent advent of high current densities in commercial electroplating of most metals has not as yet been paralleled for silver.⁶⁹

The "blue dip" into which articles of copper, brass, or tin alloys are dipped before silver plating may be made by adding to a solution containing 7.5 g. per liter (1 oz. per gal.) of mercuric chloride, $HgCl_2$, 4 g. per liter (0.5 oz. per gal.) of ammonium chloride, NH_4Cl ; or in place of the blue dip the articles may be immersed in a solution prepared by dissolving 7.5 g. per liter (1 oz. per gal.) of yellow mercuric oxide, HgO , in a solution containing 60 g. per liter (8 oz. per gal.) of sodium cyanide, $NaCN$.

Carbon bisulphide is added as a brightener. A few ounces of it are shaken up with a gallon of the plating solution containing excess cyanide. At regular intervals a definite quantity, e.g., 1 fluid oz. (30 cc.), of this solution is added to each 100 gal. of the main plating solution. If too much carbon bisulphide should be added to the plating solution, a part of it can be removed by warming the solution or bubbling air through it. The carbon bisulphide is an addition agent, and its action is not clearly understood, except that it reduces the crystal size. Articles plated in silver solutions containing no carbon bisulphide have a more coarsely crystalline, white frosted appearance and require more buffing or burnishing.

Other brighteners are gutta-percha and crêpe rubber. Pan⁷⁰ has found that sodium thiosulphate, $Na_2S_2O_3$, at a concentration of about 0.5 g. per liter (0.06 oz. per gal.), produced a brighter deposit than carbon bisulphide in the same solution.

The anodes are usually of rolled silver of high purity (999 fine) well annealed to insure uniform corrosion.

Some articles, as e.g., thimbles, are silver plated by immersion, without an external current. One solution in use is made up as follows:

36. SILVER IMMERSION SOLUTION.

	g./l.	oz./gal.
Silver cyanide, $AgCN$	45	0.5
Sodium cyanide, $NaCN$	13	1.75
Potassium hydroxide, KOH	26	3.5

Temperature, 70° C. (158° F.).

⁶⁸ N. E. Promisel and D. Wood, in *Modern Electroplating*, p. 300, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 459 (1942).

⁶⁹ L. Addicks, *Silver in Industry*, p. 273, Reinhold Publishing Corporation, New York, 1940.

⁷⁰ L. C. Pan, *Trans. Electrochem. Soc.*, **59**, 329 (1931).

An iron kettle is suitable for a container. If the article to be plated is bright, the silver finish will be bright, but it should be lacquered for protection. This method of silver plating is suitable for use on copper, brass, or bronze. Articles made of antimonial lead and aluminum-zinc alloys must previously be given a light brass plate covering.

In an attempt to avoid the tarnishing properties of silver, Stout and Thummel ⁷¹ developed a silver-cadmium alloy that is said to have practically all the desirable properties of silver without some of its limitations. Its freedom from tarnish by sulphur compounds and its cheapness as compared to silver are two of its chief characteristics. In tests of plated articles, the objects were bent repeatedly until the base metal broke, without affecting the bonding between the two metals; the deposit itself showed no noticeable failure.

The bath composition is given as follows:

37. SILVER-CADMIUM SOLUTION.

	g./l.	oz./gal.
Cadmium oxide, CdO.....	45	6
Silver cyanide, AgCN.....	3.0	0.4
Sodium cyanide, NaCN.....	124	16.5
Sodium sulphate, Na ₂ SO ₄	45	6
Nickel sulphate, Ni ₂ SO ₄ ·7H ₂ O.....	0.15	0.02
Turkey red oil.....	11.25	1.5

Temperature: atmospheric.

Current density, 0.9 to 1 amp. per sq. dm. (9 to 10 amp. per sq. ft.).

The cadmium content of the bath is maintained by the use of cadmium anodes, with an anode to cathode area of 2 : 1. The silver content is maintained by the periodic addition of a silver-sodium cyanide solution containing 75 g. silver cyanide and 90 g. sodium cyanide per liter (10 oz. and 12 oz. per gal., respectively). Too high a cadmium content can be reduced by means of Duriron anodes.

Tin Plating. The electrolytic deposition of tin has gained prominence in recent years. However, since tin can be easily applied to iron and steel non-electrolytically by hot dipping, by far the larger amount of plating is done by that means. Recently, electrodeposition of tin has been finding favor in the industries manufacturing radio parts, electric refrigerators, and dairy equipment. One firm operates more than 10,000 gal. of tin-plating solution. Tin is in itself a corrosion-resistant metal, but when plated on iron or steel it does not have the protective action

⁷¹ L. E. Stout and W. G. Thummel, *ibid.*, 59, 337 (1931).

that zinc does, for when any of the base metal is exposed the tin acts as cathode, the iron as anode, going into solution (corroding), because of local action, faster than if no tin were present. Tin-plated ware in contact with moisture has little durability, for nearly all tin plate is sufficiently porous to expose the base metal. For dairy equipment tin plate has given excellent service, probably because a thin film of butterfat coats the surface, and is not removed by the most thorough washing. For indoor work out of contact with moisture tin plate is very satisfactory. It resists most acids found in foodstuffs and is used widely in the canning industry. It provides an excellent coating for the protection of metal parts while in storage. It is used to a considerable extent as a bearing metal for plating motor pistons for "breaking-in" purposes; acting as a bearing surface it prevents seizing and consequent scouring of cylinder and piston surfaces. Tin is deposited electrolytically on steel in continuous machines, and many miles of strip steel are being electroplated for the canning industry. Solder is prepared commercially by the co-deposition of tin and lead.

Tin is plated from acid and from alkaline solutions. The alkaline bath has the higher throwing power, although the acid bath has better throwing power than most plating baths. The resistance of the alkaline bath is approximately four times that of the acid bath. The acid bath is used at room temperature; the alkaline bath must be used hot. Addition agents are important additions to acid baths.

38. TIN ACID SOLUTION.⁷²

	g./l.	oz./gal.
Stannous sulphate, SnSO_4	54	7
Sulphuric acid, H_2SO_4	100	13
Cresol sulphonic acid.....	100	13
β -naphthol.....	1	0.13
Gelatin.....	2	0.26

Temperature preferably 21 to 27° C. (70 to 80° F.).

Current density, 1.1 to 4.3 amp. per sq. dm. (10 to 40 amp. per sq. ft.).

Plating from alkaline baths has been practiced extensively since the early 1930's. The alkaline bath is especially suitable for tinning, with reasonable uniformity, fabricated articles made from a variety of metals, such as steel, copper, and bronze. Heavy deposits on odd-shaped and deeply recessed articles can be produced with greater ease and accuracy than by hot dipping.

⁷² Paul R. Pine, in *Modern Electroplating*, p. 321, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 631 (1942).

39. TIN ALKALINE SOLUTION FOR STILL PLATING.⁷³

	g./l.	oz./gal.
Sodium stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	90	12
Sodium hydroxide, NaOH.....	7.5	1
Sodium acetate, CH_3COONa	15	2
Hydrogen peroxide, H_2O_2 (100 vol.)....	0.5	1/16

Temperature, 60 to 80° C. (140 to 176° F.).

Current density, 1.08 to 2.70 amp. per sq. dm. (10 to 25 amp. per sq. ft.).

Anodes should be of pure tin.

Continuous plating of tin on steel strip received much impetus during 1942.⁷⁴ Electroplating makes it possible to control the deposit more

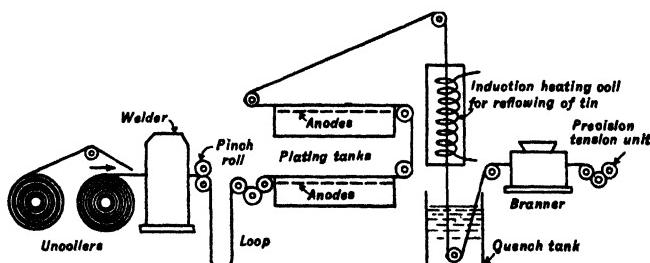


FIG. 52. Diagrammatic representation of a continuous strip tin plating line.

carefully so that approximately 65 per cent as much tin will cover a piece of steel as effectively as is required by the hot-dipping process. The continuous strip plating process speeds up plating enormously compared to the batch process of plating, for it is possible to plate a strip of steel 36 in. wide at rates up to 1,300 ft. per min.; never before has electroplating been on such an enormous production scale. A section of one type of plating line is shown diagrammatically in Fig. 52. A special feature of the process is that in each plating tank only one surface of the strip is plated. This makes it possible by proper regulation of the plating current to plate coats of different thicknesses on opposite sides of the strip. The normal operating speed is 650 ft. per min.

The tin plate produced on one of these electrolytic lines has a gray matte surface. A smooth polished surface is obtained by heating the surface of the tin so that it flows slightly and then quickly cooling it.

⁷³ F. F. Oplinger and Fred Bauch, in *Modern Electroplating*, p. 334, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 617-629 (1942).

⁷⁴ J. R. Erbe, *Westinghouse Engr.*, **2**, 117 (1942).

This reflowing not only improves the appearance but also reduces the porosity of the coating, thereby improving the corrosion resistance.

The heating of the tin is by induction. The tinned surface is brought to the melting point of the tin by the same methods now extensively employed by industry in electromagnetic heating except that the frequency and power involved are much greater. There is no physical contact between the strip and any part of the heating equipment, so that there is no marring of the surface. The space required for heating is of the order of 10 to 12 ft. at a speed of 1,000 ft. per min. Other heating methods that have been proposed are (1) passing the tinned strip through a hot oil bath, hot enough to remelt the tin, (2) passing the tinned strip through a radiant tube or some other type of furnace, and (3) using the electrical resistivity of the strip itself to heat it conductively.

A complete line uses about 25 d-c. motors from $\frac{1}{2}$ to 60 hp. The plating units require approximately 60,000 amp. at 12 volts. The total power for the line at rated load and speed is about 2,700 kw. or 3,600 hp.

The contact method of tin plating has been of importance for a long time, especially in the tin plating of small steel and brass articles such as pins, snap fasteners, hooks and eyes, and paper clips. No external current is applied, the plating depending upon local action. In one process for iron or steel articles the articles to be plated are placed in a zinc tray, or in a wire basket with a perforated sheet of zinc in the bottom. This tray or basket with its charge is placed in a tank containing the plating solution. The solution may consist of:

40. TIN SOLUTION FOR CONTACT PLATING.

	g./l.	oz./gal.
Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	25	3.3
Cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$	10	1.3

The solution is heated nearly to boiling, then allowed to cool gradually for about three-quarters of an hour, after which the plated articles are removed.

The boiling process is used especially for copper and brass articles. A wooden tank is lined with sheet brass or tin and is supplied with heating coils. The solution may have the following composition:

41. TIN SOLUTION FOR BOILING PROCESS.

	g./l.	oz./gal.
Cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$	1.5	0.2
Sodium chloride, NaCl	3.0	0.4

The solution is maintained at or near the boiling point for several hours. The articles to be tinned are placed on a perforated sheet of pure tin in a

layer about 2 in. thick. On top of this is placed another sheet of perforated tin, which in turn is covered with more ware to be plated, the top layer being also covered with tin. About a thousand pounds of articles can be plated in a tank at each boiling operation.

The tin coating is very thin, for the moment the base metal is covered with tin the plating action stops; but contrary to most deposits produced by immersion, like that of copper on iron, the tin deposit is very adherent.

The plated articles come from the plating solution with a dull color. They are subsequently tumbled in wheat bran or fine maple sawdust, after which they are tumbled in a tumbling barrel without any polishing agent.

Tungsten Plating. The present development in tungsten plating is due to the work of Fink and Jones.⁷⁵ Tungsten is in the same series as chromium in the periodic system. It has a bright silvery luster, but, unlike chromium, it is not attacked by any of the common mineral acids, including aqua regia, but is attacked by a mixture of nitric and hydrofluoric acids. Electrolytically deposited tungsten is especially valuable in covering baser metals in laboratory ware. The metal is not attacked by sulphur or phosphorus. It has a hardness on Mohs' scale of about seven. It can readily be expected that by reason of its luster, hardness, and resistance to acids and high temperature it will soon find many useful applications.

The tungsten-plating solution is easy to prepare. A saturated solution of sodium carbonate is made at 100° C. (212° F.), and tungstic trioxide, WO_3 , is added as long as the sodium tungstate formed is soluble. The solution is electrolyzed at 8 amp. per sq. dm. (75 amp. per sq. ft.), but good deposits have been obtained at 43 amp. per sq. dm. (400 amp. per sq. ft.). The higher the operating temperature, the brighter the deposit. The solution is not entirely stable on electrolysis and slowly deteriorates when used constantly. When the plating is finished, the cathode should be removed quickly and rinsed to prevent resolution of the metal by the bath.

Holt and Kahlenberg⁷⁶ have successfully plated tungsten from an alkaline phosphate solution.

Zinc Plating. Zinc may be applied as a protective coating on iron and steel by hot dipping (galvanizing), by sherardizing (in which the article is heated to 370° C. in zinc dust), or by electroplating, all resulting in excellent protection to the base metal. The protective action of zinc on iron and steel is due not only to the resistance to corrosion of the zinc, but also to its galvanic action. If any of the base metal is exposed by

⁷⁵ C. G. Fink and F. L. Jones, *Trans. Electrochem. Soc.*, **59**, 461 (1931).

⁷⁶ M. L. Holt and L. Kahlenberg, *Metal Ind. (New York)*, **31**, 94 (1933).

abrasion or porosity of the plated surface, a local couple forms, the zinc acts as anode and goes into solution, and the iron acts as cathode and suffers no corrosion as long as any zinc remains near by.

In connection with nickel plating, attention was called to the fact that, nickel being above hydrogen in the electromotive series, Table VII, the solution could be but slightly acid or hydrogen would be evolved, especially at higher current densities. Zinc is still more electronegative yet can be plated quite satisfactorily from an acid solution. This is because the overvoltage of hydrogen on zinc is high, whereas on nickel it is quite low.

Most zinc plating is done from acid or from cyanide solutions. The acid bath is used extensively in electrogalvanizing wire and strip steel. Electrogalvanized steel withstands bending and forming into special shapes, such as "BX" cable, whereas a hot-dip zinc coating cracks and flakes under like treatment.⁷⁷ Large quantities of wire cloth (screen) are galvanized in the acid bath. The outstanding characteristics of the acid over the cyanide bath are higher plating rate and lower operating costs; furthermore, the acid bath is preferred for plating on cast iron. On the other hand, the cyanide bath has greater throwing power and when properly prepared and controlled produces much brighter deposits.

42. ZINC ACID SULPHATE SOLUTION.

	g./l.	oz./gal.
Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	360	48
Ammonium chloride, NH_4Cl	30	4
Sodium acetate, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$	15	2
Glucose	120	16

Temperature, 20 to 30° C. (68 to 86° F.).

Current density, 1.5 to 3 amp. per sq. dm. (14 to 28 amp. per sq. ft.).

With solution 42, it will be necessary to add small amounts of sulphuric acid about once a day.

The zinc anodes are dissolved not only electrolytically but also chemically by the acid, so that the acid concentration decreases; it is therefore necessary to make frequent additions of acid. The action of sulphuric acid on the anodes is fast enough to decrease the acid content noticeably in a day. Weaker acids act more slowly, so that boric acid, H_3BO_3 , or acetic acid, CH_3COOH (mainly as sodium acetate, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), is added to regulate the acidity. Sodium acetate has a more pronounced buffer action than boric acid.

⁷⁷ E. H. Lyons, Jr., in *Modern Electroplating*, p. 344, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, **80**, 388 (1942).

Addition agents are used in zinc plating; they improve the quality of the deposit as well as the appearance. Corn syrup, gum arabic, glycerin, licorice, tannic acid, and tartaric acid are among those commonly used.

The anodes are cast zinc, ranging in purity up to 99 per cent. The purer anodes are much to be preferred and will ordinarily be the most economical.

In a process developed by U. C. Tainton, wire is electroplated with zinc obtained by leaching calcined zinc ores with spent electrolyte which contains free sulphuric acid. Insoluble anodes are used. The process is described on page 223 in the chapter dealing with electrometallurgy by means of aqueous solutions.

The zinc cyanide bath has come into wide use since 1935 when baths were developed capable of producing bright zinc deposits. Deposits from acid solutions are used chiefly to protect against corrosion, but the surface becomes dull. Bright zinc deposits now compete with the formerly more pleasing cadmium deposits, especially since cadmium has become more scarce on account of its use in automobile bearings. The zinc cyanide solution also has greater throwing power than the acid solution, and low-cost steel tanks can be used.

43. ZINC CYANIDE SOLUTION.

	g./l.	oz./gal.
Zinc cyanide, $\text{Zn}(\text{CN})_2$	60	8
Sodium cyanide, NaCN	52.5	7
Sodium hydroxide, NaOH	15	2
Sodium carbonate, Na_2CO_3	30	4
Sodium fluoride, NaF	7.5	1
Corn sugar.....	7.5	1
Gum arabic.....	1.1	0.15

Temperature, 40 to 50° C. (104 to 122° F.).

Current density, 4 amp. per sq. dm. (37 amp. per sq. ft.).

If the surface of cast iron contains graphite and slag, the zinc cyanide solution will not give a satisfactory deposit. Pickling cast iron will not remove the graphite and slag.

For bright zinc deposits the temperature, current density, and ratio of total NaCN to total zinc must be carefully correlated. The use of addition agents, of which a large number are covered by patents, is important; among such agents may be mentioned phenothiocyanate, methyl ethyl ketone, and molybdic oxide.⁷⁸

⁷⁸ For a discussion of bright zinc plating the reader is referred to R. O. Hull and C. J. Wernlund, in *Modern Electroplating*, p. 359-380, The Electrochemical Society, Columbia University, New York, 1942; *Trans. Electrochem. Soc.*, 80, 407-425 (1942).

Anodes of pure zinc, zinc-aluminum alloy, and zinc-mercury alloy are in use.

Brass Plating. The electrodeposition of brass is of great commercial importance. Brass is used mainly as an ornamental coating and to obtain adhesion of rubber to steel. It is plated in thin deposits, and the protective action is very slight. In commercial importance it ranks with nickel and chromium plating.

Brass, being an alloy, presents special plating problems. The plating solution must contain zinc and copper ions; these ions must be plated out in ratios of fairly definite limits, and they must be replenished from suitable anodes. By referring to Table VII, page 38, it will be noted that the normal electrode potential of zinc is -0.76 , that of copper $+0.34$. In order to plate the ions of both metals simultaneously in a satisfactory manner, it is necessary to employ cyanide solutions, in which the two metals have electrode potentials closer together. This can be accomplished by using double cyanides, and with the correct amount of free cyanide the electrode potential of copper can be made very close to or even equal to that of zinc. The effect on the electrode potential by increasing the cyanide content is shown in Table XVI.⁷⁹

TABLE XVI

EQUILIBRIUM ELECTRODE POTENTIALS OF COPPER AND ZINC IN CYANIDE SOLUTIONS

Metal	Contents of Electrolyte per Liter			
	1 equivalent metal sulphate	0.1 mole metal cyanide		
		+0.2 mole KCN	+0.4 mole KCN	+1.0 mole KCN
Zinc	-0.801 volt	-1.033 volts	-1.182 volts	-1.231 volts
Copper	+0.308 volt	-0.611 volt	-0.964 volt	-1.169 volts

It is current practice in brass plating to have the copper and zinc content of the bath in the ratio of 80 parts copper and 20 parts zinc.⁸⁰ The following bath composition will give approximately the above ratio of copper and zinc.

⁷⁹ F. Foerster, *Elektrochemie wässriger Lösungen*, p. 182, J. A. Barth, Leipzig, 1922.

⁸⁰ C. H. Proctor, *Metal Cleaning and Finishing*, 2, 25 (1930).

44. BRASS SOLUTION FOR STILL, BARREL, OR CONVEYOR PLATING.

	g./l.	oz./gal.
Copper cyanide, CuCN, 70.5% Cu....	24.5	3
Zinc cyanide, Zn(CN) ₂ , 55% Zn.....	7.5	1
Sodium cyanide, NaCN.....	37.5	5
Sodium acid sulphite, NaHSO ₃	0.12	0.016
Sodium bicarbonate, NaHCO ₃	7.5	1
Ammonium chloride, NH ₄ Cl.....	3.75	0.50
Potassium hydroxide, KOH.....	0.45	0.06
Sodium arsenate, Na ₂ AsO ₄ ·12H ₂ O....	0.075	0.01
Copper content, Cu.....	15.9	2.22
Zinc content, Zn.....	4.1	0.55

Temperature, 27° C. (80° F.).

Current density, 0.3 to 0.5 amp. per sq. dm. (3 to 5 amp. per sq. ft.).

The arsenic is used as a brightener; instead of the arsenate mentioned above, sodium arsenite, Na₂AsO₃, or arsenic trioxide, As₂O₃, may be employed. Arsenic gives a bright color to the deposit, but a solution containing arsenic is hard to control. Therefore, instead or in addition, other brighteners like ammonium chloride, ammonium hydroxide, or phenol, C₆H₅OH, are used.

Another bath composition is given below.

45. BRASS SOLUTION FOR BARREL PLATING.

	g./l.	oz./gal.
Copper cyanide, CuCN.....	27	3.6
Zinc cyanide, Zn(CN) ₂	9	1.2
Sodium cyanide, NaCN.....	54	7.5
Sodium carbonate, Na ₂ CO ₃	30	4.0
Copper content, Cu.....	19	2.5
Zinc content, Zn.....	5	0.65
Free sodium cyanide, NaCN.....	17	2.3

Temperature, 40 to 50° C. (104 to 122° F.).

Current density, 0.2 to 0.4 amp. per sq. dm. (2 to 4 amp. per sq. ft.).

The anodes should be of cast brass in preference to mixed anodes of copper and zinc. The anode does not necessarily go into solution in the same proportion as its composition, or as that of the brass in solution, or as that deposited. A common anode composition is 70 per cent copper and 30 per cent zinc. Such an anode, used in connection with solution 45 above, will give a deposit very close in color (but not necessarily in composition) to 66 per cent copper and 34 per cent zinc,⁸¹ which is the

⁸¹ C. H. Proctor, *loc. cit.*, p. 26.

composition of the sheet brass known commercially as the two-and-one mixture.

One of the difficulties in brass plating is to keep the bath composition uniform, so that the plated coat will be of a uniform color, or so to adjust the bath that the plated coat will match another coat. In a large measure, both adjustments are made by empirical methods, in the absence of definite scientific information. The field of investigation in brass plating is still a large one.

Other Alloy Plating. Brass is the only alloy that is deposited electrolytically to any considerable extent. Several alloys of gold are plated, as white gold, green gold, and red gold, and these are discussed under gold plating. A cadmium-silver alloy has some promising possibilities and is discussed under silver plating.

The electrodeposition of lead-tin alloys has been used by the U. S. Navy Department.³² The alloy is deposited from a fluoborate solution; in some respects the process is simpler than brass plating, and cathode efficiencies of nearly 100 per cent are possible over a wide range of current densities.

Bronze plating has reached commercial importance. Most bronze-plating solutions are brass-plating solutions with a high copper content so that a high-copper brass is obtained instead of true bronze (a copper-tin alloy).³³

Copper-nickel alloys, because of their similarity to Monel metals, would seem promising, but difficulty is experienced on account of the wide differences in their electrode potentials.³⁴

Plating on Aluminum. A variety of metals can be plated successfully on aluminum. Usually it is desirable to roughen the aluminum surface carefully and then to apply a preliminary coating of nickel. The desired metal can then be plated over the nickel. It is important that the composition of the aluminum alloy be taken into consideration, for the aluminum metal on which the plating is to be done may be one of a number of alloys.

The aluminum must be cleaned free from grease. Organic solvents may be used. Alkali cleaners are very satisfactory provided that the concentration of the alkali is not sufficient to mar the luster. Commercial alkali cleaners possible for other metals are too concentrated.

A satisfactory cleaner consists of 15 g. per liter (2 oz. per gal.) of sodium carbonate, Na_2CO_3 , and an equal amount of trisodium phos-

³² W. Blum and H. E. Haring, *Trans. Am. Electrochem. Soc.*, **40**, 287 (1921).

³³ C. W. Bennett, *ibid.*, **23**, 251 (1913).

³⁴ H. D. Hineline and W. B. Cooley, *ibid.*, **48**, 61 (1925).

phate, Na_3PO_4 . Its temperature should be between 82 and 93° C. (180 and 200° F.).

It is advisable to follow the alkali cleaning by an acid cleaning. A 5 per cent hydrofluoric acid, HF, solution is commonly used. It is prepared by mixing 1 part of 50 per cent acid with 9 parts of water. If the aluminum is to be plated with nickel the pickling time should be about 15 seconds; if it is to be plated with zinc the time should be 60 seconds. The hydrofluoric acid solution serves a dual purpose; it removes any remaining alkaline cleaner adhering to the surface and remedies to a small degree any slight imperfections in the alkaline cleaning. If the aluminum has but small amounts of grease on its surface the alkaline cleaning may not be necessary prior to the hydrofluoric acid dip. The acid dissolves grease and oxides on the aluminum surface. The acid cleaning is followed by a cold-water rinse.

Generally it is desirable that the surface of the aluminum be slightly roughened and that it then be plated with nickel. A satisfactory solution for roughening commercially pure aluminum (designated as 2S) consists of:

46. ALUMINUM ROUGHENING SOLUTION.

Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	270 g.	36 oz.
Hydrochloric acid, HCl, sp. gr. 1.18...	200 cc.	0.2 gal.
Water.....	1,000 cc.	1.0 gal.
Temperature.....	32° C.	90° F.

The time of dip is determined by experiment. When the dip is operating properly the aluminum comes from it with a glossy gray nickel immersion deposit resembling nickel plate. The time required is in the neighborhood of 15 seconds. The temperature and the acidity must be controlled carefully.

The aluminum is then ready for nickel plating. Many commercial nickel baths are satisfactory. Generally the baths are made up of the single nickel sulphate, sodium or magnesium sulphate, ammonium chloride, and boric acid.⁵⁵

The nickel deposit may serve as a basis for a variety of other plates. Chromium, copper, brass, and silver have been successfully applied on the nickel base.

Chromium and zinc can be plated directly on smooth aluminum. Ordinary chromium baths can be used but should be operated at double the usual current density. For zinc plating the cleaned and acid-dipped

⁵⁵ *Electroplating Aluminum*, p. 24, Aluminum Company of America, 1930; A. V. Re, *Trans. Electrochem. Soc.*, 61, 139 (1932).

aluminum is given a "flash" coating, for which the solution may consist of:

47. ZINC SOLUTION FOR PLATING ON ALUMINUM.

	g./l.	oz./gal.
Zinc cyanide, $\text{Zn}(\text{CN})_2$	30	4
Sodium cyanide, NaCN	30	4
Ammonium hydroxide, NH_4OH , sp. gr. 0.90.....	30	4
Peptone.....	0.9	$1/8$

Current density, 0.1 to 0.5 amp. per sq. dm. (1 to 5 amp. per sq. ft.).

Time, 1 to 10 minutes.

The zinc flash is followed by plating from any bath suitable for plating over zinc, but the corrosion resistance is decreased when the top coating is nickel or copper. If a resistant copper or nickel finish is desired, it should be plated on a roughened aluminum surface as explained in the preceding pages.

Plating on Glass and China. Plating on glass and china presents a special problem because the surface to be plated is non-conducting. It is therefore necessary to render conducting those parts of the surface that are to be plated. Several methods are available for this purpose. In one, an easily reducible salt of a metal is applied to the surface. For example, a concentrated solution of silver nitrate may be applied to a glass surface, and while the surface is still wet it is subjected to formaldehyde vapors which reduce the silver nitrate to metallic silver. Where no deposit is desired, the silver is wiped off. The glass is then placed in a silver-plating bath and the deposited coating is connected to the negative line. The plated deposit comes out of the bath a matte white and must then be rubbed down with a piece of polishing steel or agate. The glass may be etched by sandblasting or with hydrofluoric acid before the silver nitrate solution is applied. The surface can also be made conducting by applying a coating of graphite in an asphalt or other suitable paint, but for many purposes the black color showing through the back of the glass is objectionable. This objection can be overcome by painting the glass with a clear lacquer and allowing it to dry slightly. It is then dusted with a suitable metal bronze, for example, with copper bronze if the plated coat is to be copper. Glass can also be made conducting for silver plating by silvering the glass as for mirrors and then plating on top. The plating serves merely to thicken the deposit. Detailed information for plating on ceramic products is given by Rancke.⁸⁶

⁸⁶ C. Rancke, *Keram. Rund.*, **40**, 56 (1932).

CHAPTER VII

ELECTROREFINING OF METALS

The electrorefining of metals is one of the leading electrochemical industries. Electrolytically refined copper, in particular, is an important factor in the extensive development of the electrical industry, for all copper used for electrical conductors is refined electrolytically. Electrorefining not only produces metals of a high degree of purity but also makes possible the recovery of precious metals which are present in the ores in such small amounts that they could not be recovered practicably by any other method. A considerable quantity of gold and silver is recovered from copper and other ores that contain such minute proportions of these noble metals that their recovery alone would not be practicable. Moreover, copper is such a good collector for precious metals that it is the practice at some smelters to mix with the copper ore some silver and gold ores that could readily be handled separately. About 80 per cent of the total silver and 15 per cent of the gold production of the world are recovered as by-products from copper, lead, nickel, and cobalt refining.

The electrorefining of copper also produces nickel as a by-product, and practically all the selenium and tellurium used in this country.

Since electrorefining processes consume large amounts of electrical energy, it is natural that there was not much development along this line until after the invention of the dynamo.

General Principles. In electrorefining processes the metal to be refined is made the anode in a suitable electrolyte. It is plated out on a cathode which may be made of a thin sheet of the metal being refined, or less often of some other metal from which the deposit may later be stripped; in the series system of refining, the metal is deposited on the back of another anode.

The operating conditions are so adjusted that the metal to be refined is deposited with a high degree of purity. The more electropositive metals generally do not dissolve but remain adhering to the anode or finally drop off and form the anode mud or anode slime. The anode mud therefore consists largely of the more noble metals. If some of the electropositive metals are in the anode in relatively high percentages or if the current density is high some of these metals may go into solution,

and if they remain in solution will eventually deposit on the cathode. To prevent such contamination of the metal being refined, suitable compounds may be added to the bath that will precipitate the more noble metals. For instance, a soluble chloride added to a copper-refining solution will precipitate any silver.

The more electronegative metals readily dissolve electrolytically and will accumulate in the solution unless they also are precipitated chemically. For example, in copper refining, any lead in the anode is precipitated as lead sulphate, and any tin will precipitate slowly as an insoluble basic sulphate. Thus it is seen that some of the more electronegative metals may also be found in the slimes.

Some of the impurities, however, remain in solution in the electrolyte, and their gradual accumulation contaminates or fouls it. Their concentration may eventually become great enough for them to deposit on the cathode. It is therefore necessary to purify the electrolyte, which is usually accomplished by taking some of it from the tanks continuously and replacing it by purified solution.

COPPER

The extensive application of electrorefining of copper is due to the demands of the electrical industry, which requires a copper of a high degree of purity in order to reduce resistance losses to a minimum. Electrorefining of copper is one of the largest electrochemical industries, consuming large amounts of electrical energy. It may therefore be said that the electrical industry and the electrolytic refining of copper each helps to place the other in the important position it holds in modern industry.

A typical analysis of electrolytic copper after it has been remelted and cast into wirebars is shown in Tables XVII and XVIII, the sum of the metallic impurities being less than 0.01 per cent. These two tables represent plant results from two large copper refineries.

The greater part of the electrolytic copper produced is used for electric conductors, the electrical industry consuming more than 60 per cent of all copper produced. Therefore, the amount of allowable impurities in the refined metal is established to a large extent by their effect on the electrical conductivity, but their effect on the drawing properties of the wire and its tensile strength must also receive consideration. Antimony and arsenic up to 0.8 per cent improve the tensile properties of copper. The effect of impurities on the electrical conductivity of copper have been studied by Addicks,¹ who found that 0.01 per cent of

¹ L. Addicks, *Trans. Am. Inst. Mining Eng.*, 36, 18 (1906).

TABLE XVII

ANALYSIS OF COPPER BLISTER, ANODES, CATHODES, WIREBARS,
SLIMES, AND DORÉ METAL

	Blister	Anodes	Cathodes	Wirebars	Slimes Roasted and Leached	Doré Metal
Copper	99.00%	99.50%	99.98%	99.965%	0.50%	0.50%
Oxygen	0.25%	0.15%	0.005%	0.027%
Sulphur	.10%	.003%	.003%	.0018%	4.00%
Arsenic	.05%	.04%	.0004%	.0004%	2.50%	.01%
Antimony	.05%	.045%	.0009%	.0009%	7.50%	.01%
Selenium	.04%	.040%	.0005%	.0005%	8.00%	.05%
Tellurium	.005%	.005%	.0001%	.0001%	1.00%	.03%
Nickel	.25%	.25%	.0010%	.0010%	0.50%
Lead	.08%	.045%	.0005%	.0005%	16.00%	.05%
Zinc	.002%	None	None	None	None
Iron	.03%	0.002%	None	None	0.20%	.01%
Bismuth	.0002%	.0002%	None	None	.20%	.01%
Silica	25.00%
Silver, oz.						
per ton	30.00 oz.	30.00 oz.	0.50 oz.	0.50 oz.	0.6000 oz.	97.00%
Gold, oz.						
per ton	0.50 oz.	0.50 oz.	0.008 oz.	0.008 oz.	0.125 oz.	2.00%

NOTE: For gold and silver, 1 oz. per ton = 0.0034276 per cent.

TABLE XVIII

ANALYSIS OF COPPER ANODES, CATHODES, WIREBARS, SLIMES, AND DORÉ METAL

	Anodes	Cathodes	Wirebars	Slimes, Roasted and Leached	Doré Metal
Copper	99.349%	99.98%	99.959%	1.896%	
Oxygen		0.021%	
Sulphur	0.0027%		.0015%	1.6%	
Arsenic	.062%		.0015%	7.0%	
Antimony	.075%		.0013%	11.6%	
Selenium	.010%		.0002%	2.4%	
Tellurium	.089%		.0010%	15.3%	
Nickel	.0143%		.0021%	0.07%	
Lead	.012%		.0008%	2.8%	
Zinc	.0009%		.0007%	0.03%	
Iron	.0013%		.0023%	.03%	
Bismuth	.0054%		.0002%	1.0%	
Silver, oz. per ton	47.329 oz.		{ } 0.35 oz.	11,686.85 oz.	99.0%
Gold, oz. per ton	0.4597 oz.			113.271 oz.	1.0%

phosphorus will reduce the conductivity of copper more than 20 per cent, and 0.01 per cent of arsenic or of aluminum will reduce it more than 5 per cent. The effect of impurities on the electrical conductivity is, however, not additive. Elements which make copper brittle, such as lead, bismuth, and tellurium, have but slight effect upon the conductivity; those that make excellent bronzes, such as phosphorus, aluminum, and silicon, produce a marked depression. Silver, in the small amounts found in electrolytic copper, has no marked effect on its conductivity, so that in the A.S.T.M.² specifications, which call for at least 99.900 per cent copper, silver is counted as copper.

Since, however, electrical conductivity for copper is more important than its chemical composition, the A.S.T.M. specifications establish the maximum resistance permitted. The maximum resistance, in terms of international ohms, on the annealed copper at 20° C. (68° F.), is 0.15436 ohm per meter gram for wirebars and 0.15694 per meter gram for ingots and ingot bars.

Preliminary Treatment. Copper, like silver and gold, occurs "native," i.e., in the metallic state, but the sulphide ores are the most important sources of copper. In addition, large amounts of copper are also obtained from the oxides, silicates, carbonates, and arsenides. The ores contain on an average less than 2 per cent copper, so that usually they are concentrated by flotation or other methods, in which large amounts of worthless gangue are removed, producing a concentrate of 15 to 20 per cent copper. The concentrate, or the crude ore, if it is a high-grade ore, is roasted in a furnace to reduce but not eliminate the sulphur content. The roasted ore goes to a blast or a reverberatory smelting furnace where a large part of the remaining gangue material is eliminated, producing a matte in which all the copper exists as Cu₂S; this matte consists of the mixed sulphides of copper and iron. The gangue and some of the iron are removed as slag. The matte is placed in a converter in which air is blown through the molten bath. The air oxidizes the iron to FeO, which goes into a siliceous slag and is removed with it, and then continued blowing eliminates the sulphur as sulphur dioxide. The furnace is then poured, producing blister copper (so called from its blistered appearance caused by the escape of sulphur dioxide from the metal while solidifying) containing close to 99 per cent copper, but also containing nickel, arsenic, antimony, lead, selenium, tellurium, silver, gold, platinum, and sulphur.

The refineries generally purchase the copper as blister pigs, which are slabs about 28 by 18 by 3 in., weighing about 350 lb. each, although the refinery may also receive the copper in the form of anodes. A ton of blister copper may have a silver and gold content averaging near \$100

² American Society for Testing Materials, "Standards," Designation: B5-27.

in value, or even as much as \$500. The slabs of blister copper are therefore drilled according to a carefully planned system of templates for samples for analysis. The gold and silver tend to remain liquid longer than the copper when the cast blister slabs solidify and will therefore be more concentrated at that portion of the slab that cools last. It is therefore necessary to go to considerable pains to obtain representative samples. At the El Paso refinery of the Nichols Copper Company,³ the drillings are ground to pass an 8-mesh screen, then screened on a 40-mesh screen for coarse and fines and divided into six equal parts of each size. These are put in bags separately and sealed; they constitute the three official samples consisting of two bags each of coarse and fines. The shipper and receiver each receives one sample for analysis. If their results agree within certain limits they are accepted as final. If the results do not agree a re-assay is made by each party, and if the results still do not agree the samples are exchanged, and a re-assay is made. If there is then no agreement, the third sample is analyzed by an umpire for settlement. This general procedure is typical of all copper refineries.

The pigs of blister copper are melted and refined in the anode furnace, which is a large reverberatory furnace. The actual amounts of impurities removed in this refining furnace are small, for the cast anodes produced contain only 99 to 99.3 per cent copper, but impurities that would cause excessive fouling of the electrolyte are reduced to appreciably smaller amounts. The molten charge is subjected to an air blast, after which the slag produced is skimmed from the surface. The blowing leaves the copper saturated with cuprous oxide, Cu₂O, which amounts to about 6 per cent oxide content. This copper oxide content is then reduced by inserting long wooden poles in the melt. This whole refining process reduces the sulphur content to 0.005 per cent or less and adjusts the copper oxide content to about 2.5 per cent, the amount necessary to produce properly cast anodes. Anode furnaces have capacities of 200 to 400 tons of copper per charge. The charging, refining, and casting require about 24 hours.

The anode molds are located at the rim of a large wheel rotating in a horizontal plane. The cooled anodes are dumped automatically, and the molds continue for another cycle.

Systems of Refining. Two systems of electrolytic refining are used industrially; they are known as the series system and the multiple or parallel system. Each has certain advantages over the other; the multiple system, however, is used much more extensively.

The Multiple System. In the multiple system of refining, the anodes and the cathodes are placed in the tanks alternating with each other; and,

³ F. R. Corwin and C. S. Harloff, *Mining and Met.*, 11, 459 (1930).

in its simplest form, all the anodes are connected to the positive bus-bar, and all the cathodes to the negative bus-bar. The cathodes at the start consist of thin sheets of copper called starting sheets.



FIG. 53. Starting sheet, partially stripped. (Courtesy Baltimore Copper Smelting and Rolling Company.)

These starting sheets are themselves deposited on plates of rolled copper suspended between anodes in tanks called stripper tanks. At one plant each stripper tank contains 25 anodes and 25 blanks and takes a current density of 1.83 amp. per dm. (17 amp. per sq. ft.). At the end of 24 hr. the cathodes are removed from the stripper tanks, and the deposited copper, weighing 7 to 8 lb. for a 30-in. by 38-in. sheet, is stripped from the blank as shown in Fig. 53. In order that the deposited copper may readily be removed, the blanks are greased or oiled lightly before being placed in the stripper tank. Ears are riveted to the starting sheets so that they may be suspended as cathodes in the main plating tank.

In the earliest and simplest form of multiple connection and arrangement of cells as shown in Fig. 54, all the current required for each tank is carried by the positive and by the negative bus-bars, which requires a large investment in copper. This connection is used at present in a large western refinery. Considerable attention has been directed to arrangements that would reduce the copper required for conductors and

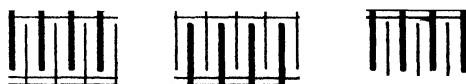


FIG. 54. Simple form of multiple connection.

that would reduce the contact resistances wherever electrodes made contact with the bus-bars or with other electrodes.

In the next development, the tanks were placed side by side instead of end to end, and a conductor was placed between the tanks, allowing the anodes of one tank and the cathodes of the next to rest upon it. It will be noted that the current carried by any one part of the intermediate

bus is but a small part of the total current. The Raritan Copper Works, in adopting this method over the old, saved about 50,000 lb. of copper⁴ used for conductors. In the earlier installations this intermediate bus consisted of a flat strip of copper, but it was found difficult to keep the contacts clean. Therefore, A. L. Walker, while manager of the Perth Amboy Plant of the American Smelting and Refining Company, changed the flat strips for ones of triangular cross-section, with the result that better contact was obtained. This system of connection, since known as the Walker system, is shown in Fig. 55 (a) and (b). However, there is

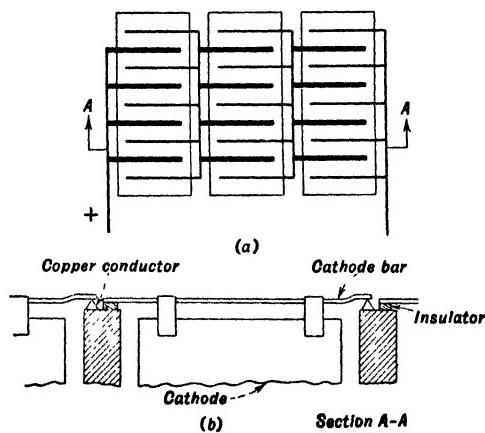


FIG. 55. The Walker system of multiple connection.

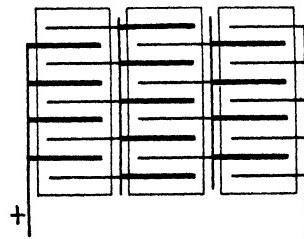


FIG. 56. The Whitehead single-contact system.

resistance loss from the cathodes to the triangular bar and from the bar to the anodes. To avoid some of this resistance, R. Whitehead, at the same plant, developed what is known as the "single contact," which permits a connection shown in Fig. 56. A triangle is cast on one lug of the anode, and the cathode bar rests upon it, thus eliminating one contact between the cathode of one tank and the anode of the next. It is still the custom, however, to rest the anode on a triangular bar merely for the purpose of equalization in the event of any irregularities within a cell. Later, P. K. Aubel, of the Baltimore plant of the same company, modified the Whitehead contact by casting a groove in one anode lug and resting a wedge-shaped cathode bar in this groove, as shown in Fig. 57.

The Series System. In the series system of refining, only the anodes are placed in the electrolyte in the tanks; i.e., no starting sheets are used. One end electrode is connected to the positive conductor, the other to the negative conductor, as shown in Fig. 58. As the current enters the

⁴ F. D. Easterbrooks, *Met. Chem. Eng.*, 6, 247 (1908).

cell through the first electrode, the electrode goes into solution and pure copper plates on the back of the next electrode; the current then passes through the metal of the second electrode and then into the electrolyte. Therefore, each electrode as it gets thinner from one side will have pure copper deposited on the back of it. The electrodes, except for the end ones, are therefore bipolar or intermediate electrodes. It is not practicable to continue the electrolysis until all the original copper has gone into solution, but the last traces of the old electrode can readily be stripped from the pure electrodes.

The series system for copper refining is employed at the Laurel Hill, New York, plant of the Nichols Copper Company where cast anodes are

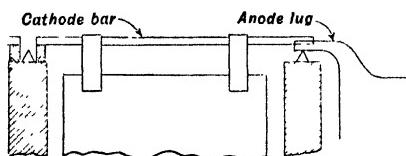


FIG. 57. The Aubel system of connecting electrodes between tanks.



FIG. 58. Series connection.

used, and at one tank room of the Baltimore plant of the American Smelting and Refining Company, where rolled anodes are used.

Comparison of the Multiple and Series Systems. The multiple system, it is claimed, will treat a relatively more impure copper than the series system, and the loss of precious metals is less. It also adapts itself better to mechanical handling of the electrodes, and owing to the greater distance between electrodes there is better circulation of the electrolyte.

TABLE XIX

COMPARISON OF THE MULTIPLE AND SERIES SYSTEMS OF COPPER REFINING

	Series System	Multiple System
Cubical contents of tanks	436 cu. ft.	175 cu. ft.
Copper tie-up in bus-bars, conductors, and starting sheets per ton daily cathode capacity	514 lb.	4,887 lb.
Anode and cathode tie-up in tank house per ton daily cathode production	41,960 lb.	53,100 lb.
Electrolyte tie-up, including storage and heating per ton daily cathode production	23,000 lb.	30,900 lb.
Floor space per ton daily cathode production	195 sq. ft.	442 sq. ft.
Current density, amp. per sq. ft. at the cathode	18-27	14-33
Current efficiency	70-75%	90-98%
Copper deposited per kw-day	250 lb. max.	100-377 lb.
Volts per tank	17	0.2-0.8
Amperes per tank	76	7,000-10,000

For the series system it is claimed that the amount of copper tied up in the plant is less because of the smaller number of bus-bars required. Less scrap is produced, less floor space is needed, and less power is required per pound of copper produced. Comparisons of the two systems are shown in Table XIX, based partly on the data given by Corwin and Harloff.⁵

Tanks. Tanks for electrolysis have been made of wood, such as Douglas fir or long-leaf yellow pine, but the tendency now is toward the use of concrete tanks. The tanks used in the multiple system, whether of wood or concrete, are lined with about $\frac{1}{8}$ in. of 6 per cent antimonial lead. For the series system of refining the lining must be non-conducting or part of the current entering the tank at the first electrode would go to the conducting lining and leave it again near the other end, thus bypassing the electrodes near the middle of the tanks. Series tanks are lined with about $\frac{3}{4}$ in. asphalt on the sides and $2\frac{1}{2}$ on the bottom.

The tanks must be sturdily constructed, for the walls of the tanks support the weight of the electrodes, which is about 10 tons for an average-sized tank. In addition, each tank will contain a little more than 3 tons of electrolyte.

The tanks generally vary in length from 8 to 14 ft., are 2 ft. 9 in. to 3 ft. 6 in. in width, and $3\frac{1}{2}$ to 4 ft. in depth. The tanks used in the series system by the Nichols Copper Company at their Laurel Hill plant are larger, being 16 ft. long, 5 ft. $4\frac{1}{2}$ in. wide, and 5 ft. $1\frac{1}{2}$ in. deep.

The tanks are preferably placed on piers of concrete or bricks of sufficient height to provide headroom of 8 to 10 ft. This gives space underneath for working during the removal of slimes and for inspection for leaks. The basement floor may be lined with mastic or with hard-burned brick laid in coal tar and asphalt.

A tank house of a copper refinery contains hundreds of electrolytic tanks. At the Raritan Copper Works, Perth Amboy, New Jersey, for instance, there are two tank houses, one of 1,800 tanks and the other of 1,656 tanks.

Tank voltages are usually under half a volt, but sufficient tanks are connected in series electrically so that the generator voltage is from 100 to 200 volts and above. Because the voltage may vary owing to cutting in and out of tanks for repairs and other causes, generators with adjustable voltage are now being supplied.

The Electrolyte. The electrolytes used in the various copper refineries are fairly uniform in composition, whether used in series or multiple systems. The electrolyte, as prepared, consists mainly of copper sulphate, introduced as blue stone, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and sulphuric acid. The

⁵ F. R. Corwin and C. S. Harloff, *Trans. Am. Electrochem. Soc.*, 57, 231 (1930).

copper content varies between 2.8 and 3.5 per cent, which corresponds approximately to between 35 and 43 g. per liter of copper or 137 to 169 g. per liter (18.3 to 22.5 oz. per gal.) of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The sulphuric acid content varies from 180 to 220 g. per liter (24 to 29.3 oz. per gal.). Sufficient free acid is added each day to take the place of that removed by the impurities and that which forms insoluble sulphates. A small amount of chloride, about 0.02 to 0.03 g. per liter, is added to precipitate the antimony (as oxychloride), bismuth, and silver. Small amounts of glue are added daily as addition agent; it helps to form smoother and denser deposits. More glue is added to the stripper tanks than to the commercial tanks. Instead of glue other organic products such as by-product sulphonates and emulsified oils have also been used.

The electrolyte gradually becomes fouled from the impurities in the anodes so that the composition of a typical electrolyte is not as simple as given above. After a certain amount of impurities has accumulated, part of the electrolyte must be removed for purification. Table XX shows the ranges of compositions of a number of electrolytes; Table XXI⁶ shows the relative distribution of the impurities between the electrolyte and the slimes.

TABLE XX

COMPOSITION RANGE OF COPPER REFINING ELECTROLYTES

Free acid, H_2SO_4	180-220 g./l.	Antimony.....	0.4	-0.6 g./l.
Copper.....	38- 45 g./l.	Iron.....	0.2	-1.2 g./l.
Nickel.....	6- 10 g./l.	Chlorine.....	0.020-0.052	g./l.
Arsenic.....	4- 12 g./l.	Specific gravity....	1.240-1.280	

TABLE XXI

APPROXIMATE DISTRIBUTION OF COPPER ANODE IMPURITIES

	In Anode Mud	In Elec- trolyte		In Anode Mud	In Elec- trolyte
Gold	100%	None	Arsenic	40%	60%
Silver	100%	None	Antimony	90%	10%
Lead	100%	None	Selenium and tellurium	100%	None
Nickel	5%	95%			
Iron	None	100%			

Operating Conditions. With one exception, already noted, all the copper anodes for the electrolytic refining are cast. For the multiple system they weigh from 500 to 700 lb. each, are 35 to 40 in. long, 28 to 36 in. wide, and $1\frac{1}{4}$ to 2 in. thick. The cast and rolled anodes of the

⁶ E. W. Rouse, Jr., "Copper Refining," *The J. E. Aldred Lectures on Engineering Practice*, Johns Hopkins University, Baltimore, 1917-18, p. 184.

series system at the Laurel Hill, New York, plant of the Nichols Copper Company weigh 104 lb. each and are 54 in. long, 12 in. wide, and $\frac{1}{2}$ in. thick. The analysis of anodes at two different refineries is shown in Tables XVII and XVIII. The multiple tanks use 22 to 38 anodes per tank, with one more cathode than anode. In series tanks the number of anodes at one plant amounts to 135 per tank. It is not practicable to continue electrolysis until all the anode is dissolved, so that anode scrap has to be removed. The scrap amounts to 6 to 15 per cent of the original weight of the anode.

In the multiple system of refining, the anodes remain in the tank from 20 to 30 days. Two crops of cathodes are generally removed during the life of one set of anodes, but in some cases three and four crops of cathodes are removed during this period. There is about $1\frac{1}{4}$ in. of electrolyte between electrodes. In the series system, where the refined copper is deposited on the back of the anodes, the electrodes remain in the tank 17 days at one plant.

The tank rooms are served by cranes that can place all the anodes properly spaced for one tank. These cranes also place the starting sheets and remove the finished cathodes, as shown in Fig. 59.

The electrolyte in the refining tanks is heated above room temperature. This has several advantages. Increased temperature decreases the resistance of the electrolyte, the temperature coefficient of resistance being about -0.5 per cent per degree F. More important, however, is the fact that increased temperature greatly improves the metallurgical conditions in the tank. The cathode deposit is firmer and denser, and the anodes corrode more uniformly. The desirable operating temperature is about 55° C. (131° F.). The electrolyte is circulated continuously through one or more tanks in series and is heated in a hot well so that it enters the electrolysis tanks at about 60° C. (140° F.). It leaves the tanks at about 50° C. (122° F.) or even lower.

The heated electrolyte, however, increases the chemical corrosion of the anodes, so that the copper sulphate content of the electrolyte increases. Copper is not ordinarily soluble in dilute sulphuric acid, but when the solution becomes aerated, as it is circulated from tank to tank, the dissolved oxygen causes slow solution of the copper, and this is augmented at elevated temperatures. The acid dissolves the cathode as well as the anode copper, so that cathode loss is about 2 per cent of that deposited, thus decreasing the efficiency by this amount.

When fairly pure anodes are being refined an excess of copper is dissolved in the electrolyte as copper sulphate which must be removed. For this purpose some of the electrolyte is withdrawn from the tank and is then treated in one of three ways. In one method the free acid is

neutralized with anode copper, and from the neutral solution, concentrated by boiling, commercial bluestone is crystallized. The copper

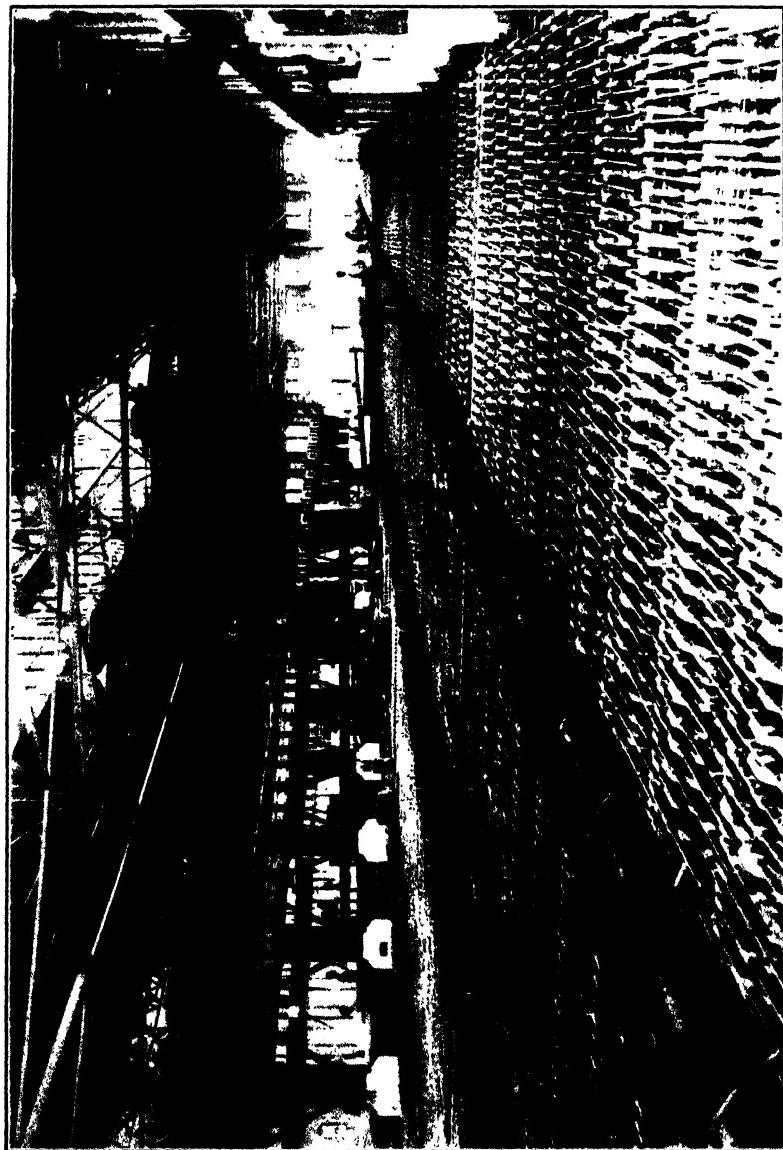


FIG. 59. Interior of a copper refinery; lifting cathodes out of tanks. (*Courtesy Baltimore-Copper Smelting and Rolling Company.*)

refineries in the United States produce bluestone having a copper content in excess of 10 million pounds. The copper remaining in the mother liquor is removed by cementation on iron. In another method,

now much less used than formerly, the copper in the electrolyte that has been withdrawn is cemented out on scrap iron directly, but the copper thus produced is impure, all the acid is wasted, and iron scrap must be supplied. In a third method the solution is placed in an electrolysis tank with lead anodes. There are generally three such tanks in cascade. The first tank operates at about 85 per cent current efficiency and produces cathodes sufficiently pure to be included with the electrolytic copper. The second tank operates at about 50 per cent efficiency and produces copper suitable for non-electrical purposes or is returned to the furnace to be melted. The last tank operates at a very low copper efficiency and produces a sludge consisting of about half copper and half arsenic. The solution when it leaves the last tank contains 0.1 per cent or less of copper and arsenic.

For the circulation of the electrolyte through the commercial tanks at the Great Falls (Montana) Reduction Department of the Anaconda Copper Mining Company, the tanks are divided into 12 sections of 120 tanks each, arranged in cascade of 5 tanks each. A separate electrolyte is maintained for each section and circulated at the rate of 5 gal. per min.

The method of removing copper in tanks with insoluble anodes is expensive, however, because the power required is about eight times as much as that used in the commercial tanks with soluble anodes. These methods of removing excess copper from the electrolyte also remove other impurities from the main tanks and are therefore classed as methods for the purification of electrolytes.⁷

If, on the other hand, the anodes carry considerable amounts of nickel, cobalt, and other impurities that dissolve electrochemically, a portion of the current is employed in dissolving these metals, but, since all the current is used in depositing only copper at the cathode, the electrolyte becomes depleted in this metal. It may even be necessary to add copper sulphate to the solution to maintain a proper copper content. In some cases as much as 2 per cent of liberating tanks with insoluble anodes must be used to remove excess copper; in others, the addition of copper sulphate is necessary. These examples represent two extremes.

The current density varies from 15 to about 27 amp. per sq. ft. (1.6 to 2.9 amp. per sq. dm.), although prior to 1916 the Great Falls (Montana) Reduction Department of the Anaconda Copper Mining Company used 40 amp. per sq. ft. (4.3 amp. per sq. dm.). The efficiency of refining decreases almost linearly with the increase in current density.

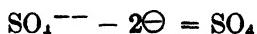
⁷ For a more complete discussion on the removal of impurities from the electrolyte, see L. Addicks, *Copper Refining*, pp. 80-100, McGraw-Hill Book Company, New York, 1921. For a general discussion on copper refining see J. Newton and C. L. Wilson, *Metallurgy of Copper*, John Wiley & Sons, New York, 1942.

A high current density decreases the amount of building equipment and the metal tie-up, but it increases the amount of gold and silver lost in the cathodes and requires a greater amount of power. Under present conditions a current density of 20 to 25 amp. per sq. ft. (2.15 to 2.7 amp. per sq. dm.) seems to strike a proper economic balance. At present, refineries operate at a current efficiency ranging from 70 to 96 per cent. It is generally desired to obtain a current efficiency not less than 90 per cent for multiple systems. The current delivered to the tanks in the multiple system ranges from 7,000 to 10,000 amp. per tank. Generally 400 to 800 tanks are connected in series.

It is necessary to keep the electrolyte in circulation through the tanks. Without circulation the heavier copper sulphate in the solution would become more concentrated at the bottom of the tanks. There would also be an impoverishment of copper ions at the cathodes and an increase of copper ions and therefore of copper sulphate at the anodes, so that the concentration might be sufficient for the salt to crystallize on the anode if the acid concentration were high. The anode will then act as an insoluble anode, i.e., instead of the reaction



the reaction will be, in part at least,



The result is that a higher voltage will be required, and the copper concentration of the electrolyte will be lowered. The solution is therefore drawn from the tanks and passed through a hot well, bringing the

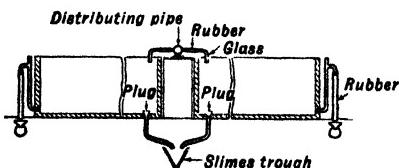


FIG. 60. Pipe connections to copper refining tanks.

temperature back to about 60° C. (140° F.). By means of centrifugal pumps or a Pöhlé air lift the solution is pumped either directly to the electrolysis tanks or to an overhead storage tank from which it is conducted by gravity to the various tanks. It has generally been the prac-

tice to introduce the solution at the bottom of the tanks and to withdraw it at the top. In this method the flow of the electrolyte is opposite to the settling of the slimes. If the rate of circulation is too great the slimes will be stirred up, so that the rate of circulation has been limited to about 5 gal. per min. In order to permit better settling of the slimes one plant is using a downward system of circulation, as shown in Fig. 60.

Anode Impurities. The impurities found in the copper anodes will find disposition in three possible places: (1) in the anode mud, (2) in the electrolyte, and (3) in the cathodes. All the insoluble impurities help to form the anode mud or slimes. A number of the impurities remain in solution, and some of these, if a high current density is used, may deposit on the cathode electrolytically. In addition, some of the anode mud may be occluded in the cathode copper. Selenium and tellurium occur in the anode combined with silver, and if there is not enough silver to satisfy these two elements, the remainder is combined with copper; these compounds are insoluble and go into the anode mud. Lead dissolves at the anode but is precipitated by the acid of the electrolyte as lead sulphate, $PbSO_4$. Arsenic also dissolves in the electrolyte as arsenious oxide, As_2O_3 , and antimony as antimonicous acid, H_3SbO_3 . The two will combine to some extent as a light basic precipitate, forming troublesome "float slimes." All anodes contain some sulphur and also some oxygen combined with copper; these insoluble compounds settle to the bottom. In addition, some copper is loosened mechanically from the anodes and drops into the mud. Some copper dissolves electrolytically as univalent ions, which form divalent copper ions and atomic copper as follows:



This precipitated copper also settles to the bottom.

The anode mud or slimes is equal to $\frac{1}{2}$ to 3 per cent of the weight of the anodes. One large western refinery produced 102 tons of anode mud per month.⁸ The slimes provide a large part of the world's supply of gold and silver, and all the selenium and tellurium. The recovery of the gold and silver will be discussed later in this chapter. Table XXII shows the range of composition of a number of slimes.

TABLE XXII

COMPOSITION RANGE OF COPPER ANODE SLIMES, UNROASTED AND UNLEACHED

Gold.....	0.0548	- 0.6855%	(16-200 oz./ton)
Silver.....	10.28	- 15.07%	(3,000-14,900 oz./ton)
Copper.....	16	- 24%	
Nickel.....	0.05	- 5.25%	
Lead.....	1	- 16%	
Antimony.....	2.3	- 8%	
Tellurium.....	0.8	- 6%	
Selenium.....	1.5	- 9%	
Arsenic.....	2.7	- 3.9%	
Bismuth.....	0.26	- 0.46%	
Iron.....	0.17	- 0.27%	

Anode mud, proportion of anode weight, 0.4-1.5%.

⁸ W. T. Burns, *Eng. Mining J.*, 122, 311 (1929).

The slimes are removed from the tanks before a new set of anodes is introduced. The electrolyte is allowed to clarify for an hour and is then drawn from the tanks, and the slimes are sluiced out through a hole in the bottom of the tank along a trough leading to the collecting tank. Figure 60 shows the arrangement for removing the slimes.

Antimony will dissolve in the electrolyte to the extent of about 0.35 g. per liter. The solubility of antimony is controlled by the introduction of a chloride which causes the antimony to precipitate as antimony oxychloride. If the antimony content is not properly limited it is the most troublesome of all the impurities, but fortunately the amount is easily controlled. The troublesome impurities in the electrolyte are arsenic and nickel, and sometimes bismuth, and it is on account of these that the electrolyte must be purified from time to time. The higher the concentration of these impurities in the electrolyte, or the greater the current density used, the greater will be the relative amounts in which they are found in the cathodes. It is desirable to keep the sum of all the impurities in the electrolyte below 25 g. per liter.

Disposition of the Copper Cathodes. The pure copper cathodes are melted in large reverberatory furnaces, where they undergo a melting process similar to that in the anode furnaces. Because the greatest part of the melted copper is cast into bars ready for rolling and drawing into wire, the furnaces are called "wirebar furnaces"; they are also known as "refining furnaces," but this is a misnomer, for the copper actually becomes slightly contaminated as shown in Tables XVII and XVIII, page 161. The poling process is conducted carefully to adjust the oxygen content to the proper point, which is determined by microscopic and macroscopic examination of solidified samples before the bars are cast.

Brass companies through the introduction of electric furnaces have been able to use larger copper shapes than the customary ingots, and consequently brass making is now carried on almost exclusively with cathodes as the furnace charge, thereby saving the melting cost at the refineries. The series cathode is of suitable size for direct use in the furnaces; the multiple cathode is usually sheared into six pieces before charging into the furnace.

Slimes Treatment.^{9, 10} Slimes, also called anode mud, are a concentrated product of the insoluble impurities found in the anodes, containing also some copper as explained previously. The slimes are valuable for their content of the noble metals as shown in Table XXII, page 173.

⁹ E. W. Rouse, Jr., *op. cit.*, p. 136.

¹⁰ *The Raritan Copper Works*, a 24-page pamphlet issued by the Raritan Copper Works, Perth Amboy, New Jersey.

Their value in some cases exceeds \$16,000 per ton of dry slimes, and care is taken to avoid loss. The dry material is very fine and a portion may easily be lost as dust. The slimes furnaces are connected to an elaborate flue system or to a Cottrell system of electrical fume precipitation. The flue dust is especially rich in selenium.

The slimes are filter-passed or filtered through an Oliver filter, forming a dense cake containing about 35 per cent moisture. The copper is then removed by first converting it to oxide by roasting at about 300° C. (572° F.) and then leaching with a 10 per cent sulphuric acid solution. In place of the roasting process the trend now is toward oxidizing the copper by blowing hot air through the damp filter cake. Either treatment reduces the copper content to less than 1 per cent after leaching. The leached slimes are again filtered and then melted in small reverberatory (*doré*) furnaces where the base metals are removed as slag. Lead, if present, forms a lead slag which is skimmed off. Antimony oxidizes and likewise dissolves in the lead slag, although a small amount goes into the flue dust. These slags are sent to a lead refinery where they are treated for recovery of lead and antimony and some silver that is carried along. Selenium and tellurium are partly volatilized, but the greater part is removed in an alkaline flux consisting of sodium nitrate and either sodium carbonate or sodium hydroxide. The alkaline slags are treated for removal of silver, gold, and small amounts of arsenic which they contain. This treatment is usually carried on within the copper refinery, and the silver-bearing residues are returned to the process. This furnace produces a bullion consisting essentially of gold and silver, but it may also contain platinum and palladium. This bullion is called "*doré*"; typical analyses of it are shown in Tables XVII and XVIII, page 161.

The *doré* may be parted by sulphuric acid or by an electrolytic method. In the acid parting method the *doré* is boiled in 66° Bé. (96–98 per cent) sulphuric acid in cast-iron kettles. The silver sulphate liquid is siphoned into a tank of water, and the solution is boiled. Copper plates hung in the tank precipitate the silver. The precipitated silver is washed, dried, melted, and then cast as refined silver.

The electrolytic parting methods will be described in subsequent parts of this chapter under silver and gold refining.

The platinum metals go into the slimes along with the gold in the electrolytic parting and are recovered by a somewhat complicated chemical process.

SILVER

A large part of the silver produced is obtained from the slimes which are a by-product from the electrorefining of baser metals, especially from

the refining of copper, lead, nickel, and zinc. Other sources of silver for electrorefining are the silver concentrate obtained when lead is desilverized by the Parkes process, silver-gold bullion of various composition, and scrap. Gold and silver are nearly always found associated, so that the refining is also a parting process for the two metals.

The slimes from the copper refinery, for example, are melted and cast into anodes and are sent to the silver refinery for electrolytic parting. The metal obtained from smelting of the slimes is called doré metal; besides about 95 per cent silver and 3 per cent gold, it may contain some

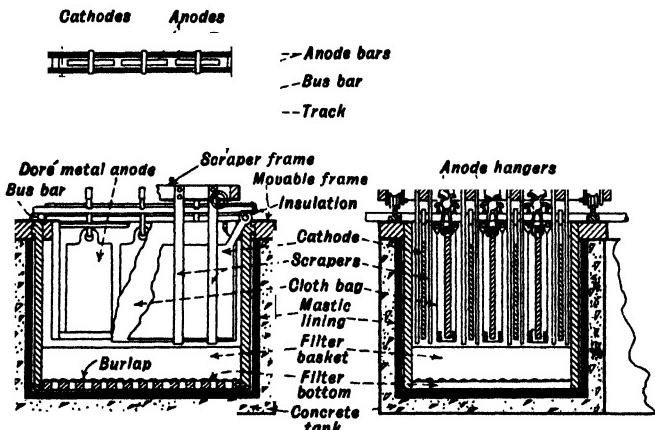


FIG. 61. Moebius cell for silver refining.

copper, lead, bismuth, cadmium, nickel, iron, tellurium, platinum, and palladium.

The two principal electrolytic methods for parting silver and gold in doré bullion are the Moebius and the Thum processes. In either method, the silver is deposited as loosely adhering crystals on the cathode, and the gold is collected as anode mud or slimes.

The Moebius cell,¹¹⁻¹⁵ shown in Fig. 61, was first used at the Kansas City Smelting and Refining Company, Argentine, Kansas, in 1885. The cell is made of acid-proof stoneware or mastic-lined concrete 24 by 26 by 22 in. deep. The cell illustrated contains three sets of anodes, three anodes to a set. Each anode is 14 by 5½ by ¾ in. thick and weighs 100 oz. The anodes consist of about 95 per cent silver, the remainder being mainly copper and gold. There are four cathodes to a

¹¹ F. D. Easterbrooks, *Trans. Am. Electrochem. Soc.*, **8**, 125 (1905).

¹² E. F. Kern, *Met. Chem. Eng.*, **9**, 443 (1911).

¹³ *Annual Report of the Director of the (U. S.) Mint*, 1912, p. 50.

¹⁴ G. G. Griswold, *Trans. Am. Electrochem. Soc.*, **35**, 251 (1919).

¹⁵ Chemnitz, *Chem. Zentr.*, **52**, 385 (1928).

cell, made of rolled silver $\frac{1}{32}$ in. thick or of stainless steel. The anodes are surrounded by canvas bags to prevent the anode mud from mixing with the deposited silver. The arrangement of the electrodes is similar to that in the multiple system in copper refining.

The electrolyte is a neutral solution containing generally 60 g. silver per liter as silver nitrate, but cells have been operated commercially using as little as 15 g. silver per liter. The electrolyte also contains 30 to

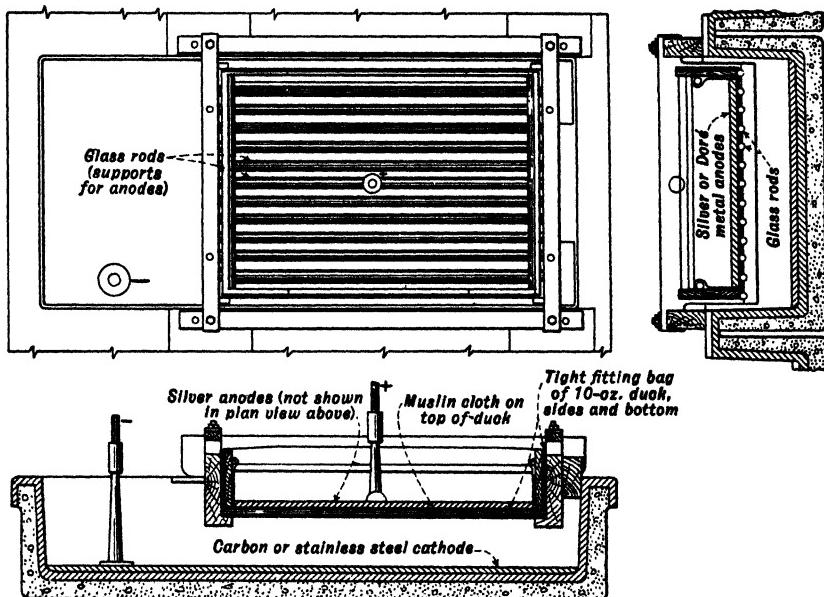


FIG. 62. Thum cell for silver refining.

40 g. copper per liter as cuprous nitrate. Part of the electrolyte is withdrawn from each cell daily and replaced by fresh electrolyte. In this way the impurities in the electrolyte are kept below a certain maximum. The waste electrolyte is first treated with copper, on which the silver precipitates, and then with iron on which the copper precipitates (cements).

The cells operate at 50 amp. per sq. ft. (4.6 amp. per sq. dm.), which requires about 450 amp. per cell, at 2.7 volts.

Between the anodes and cathodes, wooden scrapers move back and forth, stirring the electrolyte and knocking crystals of deposited silver from the cathodes. The crystals collect on a tray in the bottom of the cell below the electrodes and are removed several times a day. The crystals are washed and then melted in graphite crucibles and are cast into bars weighing 1,000 oz. The bars assay above 999 fine.

The slime, amounting to 1 to 2 per cent of the weight of the anodes, collects in the bags surrounding the anodes. It contains all the gold, platinum, and palladium, and is removed every few days. It is washed and treated with sulphuric acid in iron boiling kettles to remove copper and silver. It is then washed, dried, and cast into anodes for refining electrolytically by the Wohlwill process for gold refining.

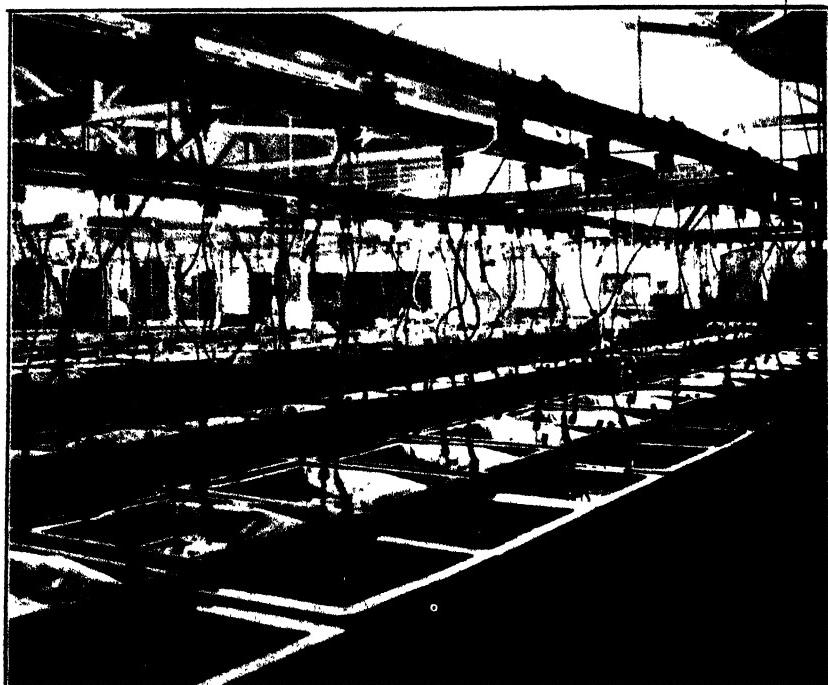


FIG. 63. An installation of Thum cells for silver refining. (*Courtesy Raritan Copper Works.*)

The Thum cell,^{16, 17} shown in Fig. 62, consists of a shallow tank, about 52 by 24 by 9 in. deep, made of acid-proof stoneware or of concrete, mastic lined. The cathode consists of a slab of carbon or graphite placed horizontally, covering the entire bottom of the cell. Five anodes of doré bullion, about 8 by 12 in. each, rest horizontally on the bottom of a wooden or stoneware basket placed above the cathode, with a piece of muslin or duck placed in the bottom of the basket under the anodes. This muslin serves as a diaphragm to prevent the gold slime from falling on the silver deposited on the cathode below. Electrical contact is made with both electrodes by a silver plate with vertical lugs.

¹⁶ F. F. Colcord, *Trans. Am. Electrochem. Soc.*, **49**, 351 (1926).

¹⁷ *The Raritan Copper Works.*

The composition of the electrolyte and the current density are the same as for the Moebius cell. The voltage, however, is greater, about 3 to 3.5 volts, owing to slime settling on the muslin below the anodes. The anode charge lasts about 96 working hours. The gold slimes are collected from the muslin diaphragms every five days. The silver, deposited on the horizontal cathode in a loose crystalline form, is scraped periodically from the cell with an aluminum hoe. The subsequent melting of the silver and the treatment of the gold slimes are the same as described under the Moebius cell. An installation of Thum cells is shown in Fig. 63.

The Moebius cells require a smaller floor space and less energy per unit silver produced, and they consume less nitric acid than the Thum cells. There is, however, appreciable anode scrap that cannot be consumed in the cell without recasting. The scrap amounts to about 15 per cent of the weight of the anodes, and if the anodes contain a relatively large amount of metal other than silver, the scrap may be considerably more. In the Thum cells the anodes are consumed completely. Any anode fragments, including those from the Moebius cells, are placed in the basket under new anodes and are thus dissolved.

Because of the position of the electrodes, these two types of cells are also called vertical and horizontal cells, respectively. Both types are used extensively commercially and by the United States Mint.

GOLD

The electrolytic process for gold refining, developed by Wohlwill^{18, 19} in Germany, was first used in 1878; it is now universally adopted. It consists essentially of electrolyzing impure gold anodes in a hot acid solution of gold chloride.

The anodes may be impure gold bullion or made from the anode mud from the electrolytic refining of silver. The anodes generally contain from 94 to 98 per cent gold, and in addition such metals as silver, which may constitute as much as 5 per cent, and copper, lead, platinum, and palladium. If the anodes are obtained from the anode mud of silver refineries, any remaining silver is generally removed by a sulphuric acid parting method. It is on account of the copper that a cyanide solution cannot be used, for the copper would plate out with the gold. Gold, copper, lead, platinum, and palladium dissolve anodically. Silver and any iridium, rhodium, and ruthenium remain in the slimes, the silver as silver chloride. The anodes used at the United States Mints are about

¹⁸ D. K. Tuttle, *Electrochem. Ind.*, **1**, 157 (1903).

¹⁹ E. Wohlwill, *ibid.*, **2**, 221 (1904), and *Electrochem. and Met. Ind.*, **6**, 450 (1908).

$\frac{1}{2}$ in. thick, but those at private refineries are much thinner. They are suspended on gold hooks, the hooks themselves not being submerged, to prevent their solution. The cathodes consist of thin sheets of gold foil and are of the same shape as the anodes. A number of anodes and cathodes are connected in multiple as in copper refining.

The electrolyte contains 7 to 8 per cent gold as chloride, AuCl_3 , and 10 to 16 per cent hydrochloric acid. It is operated at about 70° C. (158° F.) at a current density of 11.8 to 12.9 amp. per sq. dm. (110 to 120 amp. per sq. ft.) which requires about 1.3 to 1.5 volts per cell.

Part of the electrolyte is removed for purification and is replaced with fresh electrolyte. The gold is removed from the electrolyte by sulphur dioxide or ferrous sulphate solution,²⁰ and the platinum is precipitated by ammonium chloride as ammonium chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$. Palladium, if present, is removed with sodium hydroxide after evaporation to dryness; the copper is removed with iron scrap.

The slimes contain gold, amounting to about 15 per cent of that deposited on the cathode, silver chloride, lead sulphate, and the rarer platinum metals. The lead sulphate is removed by treatment with sodium carbonate solution, followed by nitric acid; the silver chloride is fused and poured off, then reduced and returned to the silver refinery. The residue from the slimes is recast into fresh anodes.

The cells are made of glazed porcelain or acid-proof stoneware, and on account of the expensive nature of the electrolyte are small in size. The tanks at the Philadelphia mint are 15 by 11 by $8\frac{1}{4}$ in. deep.

The gold cathodes produced are about 999.80 fine, or very nearly 24 karat.

If the anodes contain silver, the silver chloride formed adheres to the anodes in the form of a film and introduces operating difficulties. Wohlwill²¹ found that if alternating current is superimposed on the direct current the silver chloride does not collect on the anodes.²² It is thus possible to use anodes containing 15 per cent silver instead of only 8 per cent.²³ The amount of gold dissolved and deposited is a function of the direct current only, but the power consumption is equal to the sum of both currents.

The superimposed alternating current in addition to flaking off the silver chloride from the anode serves other useful purposes: it reduces the actual e.m.f. of the cell; it prevents liberation of chlorine at the

²⁰ A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, p. 301, Edward Arnold and Company, London, 1924.

²¹ German Patent 207,555, September, 1908.

²² Anon., *Met. Chem. Eng.*, 8, 82 (1910).

²³ E. Downs, *J. Electroplaters' and Depositors' Tech. Soc.*, 5, 51 (1930).

anode; it allows the use of a higher current density; less gold is left in the anode sludge; and the electrolysis may be conducted at a lower temperature.

NICKEL

The world's supply of nickel is obtained largely from the Sudbury nickel field, Ontario, Canada, and from New Caledonia, an island east of Australia, the Canadian field producing more than 90 per cent of the total.

The nickel in the Canadian ore is associated with copper, being present mainly as pentlandite, $(\text{Fe}, \text{Ni})\text{S}$. The ore averages about 3 per cent nickel and 1.5 per cent copper.

Preliminary Treatment. The ore is generally given a roasting which reduces the sulphur from 25 per cent to 10 per cent. It is then smelted in a reverberatory or a blast furnace to which a small amount of flux and about 10 per cent of coke are added. The nickel collects in the matte, which contains all the nickel and copper, most of the sulphur, and more than half of the iron. The slag contains all the silica, magnesia, lime, and alumina.

The matte is treated in a converter, where, by a process of oxidation and slagging, a high-grade matte is obtained, consisting of approximately 37 per cent nickel, 42 per cent copper, 20 per cent sulphur, and 0.3 per cent iron.

Several methods are available for further refining of this Bessemer matte. These are: (1) the Orford or "tops-and-bottoms" process, which may or may not be followed by electrolytic refining, used by the International Nickel Company; (2) the Mond or carbonyl process, used at Clydach, Wales; and (3) the Hybinette process of electrolytic refining, formerly used by the British-American Nickel Company, at Deschenes, Quebec. Only the first and third method will be discussed here.

The Orford or tops-and-bottoms process is based upon the fact that, when nickel, copper, and sodium are fused together, two layers are formed. The upper layer contains most of the sodium, copper, and iron, as double sulphides, and is called the "tops." The lower layer, or "bottoms," contains most of the nickel as sulphide, Ni_3S_2 . Therefore, the Bessemer matte is charged into a blast furnace with sodium sulphate, Na_2SO_4 , or crude niter cake, NaHSO_4 , and coke. The molten matte is drawn off into cast-iron pots to cool. A sharp separation takes place, but the first separation is not complete. The "tops" contains about 90 per cent of the copper; the bottom layer is remelted, giving a fairly good separation of the nickel and copper sulphides.

The nickel sulphide is washed with water to remove the sodium sulphide and with sulphuric acid to remove the iron, although this last step may be omitted. It is then given a chloridizing roast at 750 to 800° C. (1,382 to 1,472° F.) which puts the copper in a soluble form as cuprous chloride, Cu_2Cl_2 , and oxidizes the nickel to the oxide, NiO . The copper is leached out, and the remaining material, known as green nickel oxide, contains about 74 per cent nickel and 0.1 per cent copper. It is then given a second roast with soda ash, Na_2CO_3 , which removes more impurities and converts the nickel to the black oxide, NiO , of the composition 77.8 per cent nickel, 0.1 per cent copper, and from 0.005 to 0.010 per cent sulphur.

The International Nickel Company Process for Nickel Refining. The largest electrolytic nickel refinery in the world is operated by the International Nickel Company at Port Colborne, Ontario, on the northern shore of Lake Erie. The process has been described by Peek.²⁴

The electrolyzing tanks are made of concrete with 6-in. walls, lined with mastic $1\frac{1}{2}$ in. thick. The inside dimensions of the tanks are 2 ft. $10\frac{1}{2}$ in. by 16 ft. $9\frac{1}{2}$ in. by 5 ft. 2 in. deep. Two units contain 104 tanks each, and 4 units contain 156 tanks each.

The anodes are cast in cast-iron molds and measure 27 by 36 in. below the lugs. They are of irregular thickness and average 425 lb. each. The lower sides of the lugs are ground bright to make good electrical contacts on the tank bus-bars. There are 29 anodes to a tank.

The cathode starting sheets are made of nickel. They are prepared in separate tanks by electrodeposition of nickel on aluminum starting blanks from which they are stripped. In order to prevent the nickel from depositing around the edges of the aluminum sheets, wooden sticks 1 in. square are applied to the sides and bottom. The finished nickel starting sheets are 28 by 36 in. and weigh about 11 lb. each. There are 30 cathodes to a tank, which gives an active cathode area of about 405 sq. ft. per tank. The finished cathodes weigh about 128 lb. each.

Each cathode is placed in a "box" or chamber, which consists of a spruce wood frame for ends and bottom and heavy canvas duck for sides parallel to the faces of the cathodes. Along the outer side of each tank is a hard-rubber header along the top, connected at its center to the pure solution main by means of a rubber hose. The header carries 30 hard-rubber nipples, to each of which is attached a $\frac{1}{4}$ -in. soft-rubber feed pipe to lead pure electrolyte to the cathode boxes.

The purified electrolyte entering the cathode boxes contains nickel sulphate, $NiSO_4$, equivalent to about 40 g. nickel per liter, and about 20 g. per liter boric acid, H_3BO_3 . Copper and iron should each be less

²⁴ R. L. Peek, *Eng. Mining J.*, 130, 482 (1930).

than 0.005 g. per liter, and a hydrogen-ion concentration equivalent to pH 4.8 to 5.2 is satisfactory.

The impure electrolyte leaves the anode compartments and passes into preheater tanks where it is heated to 82° C. (180° F.) by steam coils. The electrolyte then flows through a series of either 6 or 8 cementation tanks for the removal of copper. The cementing agent is powdered nickel obtained by the reduction of green oxide with water gas, about 7,000 lb. being used in each tank. The de-coppered solution flowing out of the last cementation tank goes to a Dorr thickener. The underflow from the thickener, consisting largely of metallics suspended in 10 times their weight of solution, is pumped back to the first cementation tank, while the overflow goes through a train of 4 blow-tanks where air is blown through the solution to oxidize the iron which is then precipitated as ferric hydroxide, $\text{Fe}(\text{OH})_3$. A suspension of nickel carbonate, NiCO_3 , in water is fed in to neutralize the acid set free by the hydrolysis of ferric iron. After leaving the blow-tanks the solution is filtered in wooden plate-and-frame filter presses. The clear filtrate flows to head tanks, then *via* regulating boxes and wooden flow pipes to the cathode chambers of the plating tanks to complete the cycle.

The electrolyte flows from the cathode chambers through the diaphragms into the anode chambers at a rate greater than the velocity of the ions so that impurities dissolved from the anodes do not reach the cathodes. Nickel ions formed as a result of solution of the anode have to travel from the anode compartment through the heater, the cementation and iron-removal process, and back to the cathode compartment before they are discharged on the cathode.

The operating voltage is about 2.4 volts per cell with 4,800 amp. per tank, which corresponds to about 11.8 amp. per sq. ft. (1.27 amp. per sq. dm.). The operating temperature is about 57° C. (135° F.). The cathode current efficiency is about 98 per cent.

The completed nickel cathodes, averaging about 128 lb. each, are washed and then soaked over night in warm water to insure removal of nickel salts. The whole cathodes are shipped as such or are cut into squares ranging from 2 to 9 in. on a side and packed in wooden barrels holding from 1,000 to 1,500 lb. each.

The anode slime in part falls to the bottom of the cell, whence it is removed periodically, and in part adheres to the anode scrap. The slime may adhere tightly to the scrap so that scrubbing with a stiff broom is necessary. It is then washed off with a stream of electrolyte. The slime is filtered in a wooden plate-and-frame filter press. The press cake is calcined in furnaces, which reduces the sulphur content to about 0.2 per cent, after which it is melted with coal in an electric furnace.

The metal is cast in regular anode molds forming secondary or precious-metal anodes, containing about 24 per cent copper and 73 per cent nickel. These are electrolyzed in regular tanks used especially for that purpose. In order to prevent loss of the very high-grade slimes obtained from these secondary anodes, the anodes are wrapped in closely woven cotton duck. The secondary slime contains about 2 per cent of the platinum-group metals, which is soldered up in steel cans and shipped to the platinum refinery in Acton, England.

The Hybinette Process for Nickel Refining. The Hybinette process was developed by V. N. Hybinette in Norway and later introduced into America by the British American Nickel Corporation, and was in use for some time. The matte from the Bessemer converters was granulated and roasted, reducing the sulphur content from 20 per cent to 5 per cent.²⁵ It was then leached with a 10 per cent sulphuric acid solution which removed a large part of the copper but little of the nickel.²⁶ The residue was melted and cast into anodes 24 in. by 36 in., containing about 65 per cent nickel, 27 per cent copper, and less than 0.5 per cent iron.

The leach solution from the roasted matte, containing copper, was denuded of its copper content in electrolysis tanks with insoluble anodes. The electrolyzed solution, depleted of its copper, contained sulphuric acid which had been regenerated; it was returned to the leaching plant to dissolve more copper from the roasted matte.

The anodes, 36 in number, were placed in lead-lined tanks. Each anode was encased in a special canvas-bag diaphragm to catch the anode slime. The cathodes consisted of plates of copper or iron painted with graphite from which the deposited nickel could later be stripped. Each cathode was suspended in a wooden frame covered with canvas to serve as diaphragm.

The electrolyte contained 45 g. nickel per liter. The pure electrolyte was introduced into the "Hybinette bags" surrounding the cathodes, where part of the nickel was deposited on them. Owing to the hydrostatic pressure, the electrolyte flowed through the diaphragms toward the anodes, where the removed nickel was replenished from the anodes. Copper was introduced as the anodes dissolved, but because of the flow of the electrolyte it never reached the cathodes. The anolyte, containing copper and nickel, was piped to cementation vats containing anode scraps, where by a cementation process the copper in the electrolyte was precipitated and nickel was resupplied to the solution. The purified electrolyte was piped to the main nickel refining cells, where it again

²⁵ Royal Ontario Nickel Commission Report, Appendix, p. 83, 1917.

²⁶ J. L. McK. Yardly, *Eng. Mining J.*, 114, 810 (1922).

entered the cathode chambers. The scrap anodes were just about sufficient in quantity for the cementation process.

The cathodes contained approximately 98.6 per cent nickel and cobalt, 0.02 per cent copper, 0.07 per cent iron, and 0.04 per cent hydrogen.²⁷

It has not been possible completely to separate cobalt and nickel electrolytically; a closer separation is obtained in the carbonyl process.

It will be noted that the International Nickel Company process previously described is essentially the Hybinette process worked on Orford-process bottoms.

A process has been described by Bogitch²⁸ which uses a nickel chloride, NiCl_2 , solution for electrolyte. The anodes contain about 10 per cent of copper, plus iron, sulphur, arsenic, and oxygen, and yield a cathode containing 99.9 per cent nickel plus cobalt. The cell is operated at a temperature of 65° C. (150° F.). The electrolyte, having a specific gravity of 1.2 (about 230 g. per liter nickel chloride), flows from the cathode chamber to the anode chamber and then to the purifying tanks, where nickel hydroxide, Ni(OH)_3 , is added to precipitate the iron, arsenic, and cobalt. The deposit peels from flat starting sheets, but satisfactory results are obtained when the nickel is deposited on a pure nickel wire 0.5 mm. in diameter. The cathodes are removed as bars 50 to 60 cm. long and 15 to 20 cm. in diameter, and after a softening annealing are cut into small cylinders.

LEAD

The electrorefining of lead has been limited to some extent by the fact that pyrometallurgical methods of refining are simple, cheap, and capable of producing a product of 99.99 per cent lead plus bismuth. For many purposes a small amount of bismuth has no detrimental effect. However, some lead contains objectionable quantities of bismuth, and electrorefining processes produce marketable lead from such bullion. For most purposes silver is not objectionable in lead, but it is objectionable if the lead is to be manufactured into white lead.

All electrolytic refining of lead is done by the Betts process,²⁹⁻³² in

²⁷ R. L. Peek, personal communication.

²⁸ B. Bogitch, *Compt. rend.*, **188**, 328-9 (1929).

²⁹ A. G. Betts, Electrolytic refining of lead and lead alloys, U. S. Patent 713,277, Nov. 11, 1902; Electrodeposited lead, U. S. Patent 713,278, Nov. 11, 1902. U. S. Patents 891,395, June 23, 1908; 891,396, June 23, 1908; and 918,647, April 20, 1909, also by Betts, deal with the treating of anode slimes.

³⁰ A. G. Betts, *Lead Refining by Electrolysis*, John Wiley & Sons, New York, 1908.

³¹ A. G. Betts, *Electrochem. Ind.*, **1**, 407 (1903).

³² P. F. McIntyre, *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 271 (1936).

which anodes of lead bullion and starting sheets of electrolytic lead are connected in multiple as in the electrorefining of copper. The electrolyte consists of a solution of lead fluosilicate, PbSiF_6 , and free hydrofluosilicic acid, H_2SiF_6 .

The electrolytic lead refineries in North America are the Consolidated Mining and Smelting Company, Trail, British Columbia, and the United States Metal Refining Company, East Chicago, Indiana. Plants are also located in Peru, England, and continental Europe. It was once considered necessary to use electrolytic refining for bismuth-bearing bullion, because it removes and recovers the bismuth as well as gold and silver from the lead. However, the calcium debismuthizing process has been supplanting the electrolytic refining methods for removal of bismuth, gold, and silver from the lead.

Reduction of the Ore. The most important lead ore is the ore containing lead sulphide or galena, PbS . The ore as it is removed from the ground contains about 4 to 11 per cent lead; but before metallurgical treatment it is necessary to concentrate the ore to 50 to 80 per cent lead. The concentrates are roasted to oxidize and volatilize the sulphur and some of the other impurities. The roasted ore may be reduced in several different types of furnaces, but the blast furnace is used most commonly. The blast-furnace charge consists of the roasted ore, coke, and a flux. The products of the blast furnace are lead bullion, which contains practically all the lead and some of the gold and silver; matte, which is made up of the sulphides of lead, copper, iron, and the precious metals; and the slag, which is usually discarded. The bullion as produced in most of the smelting centers of the United States contains from 40 to 500 oz. of silver per ton, up to 2 oz. of gold per ton, and small amounts of copper, arsenic, antimony, sulphur, and zinc. The bullion is softened (i.e., the major part of the impurities, particularly copper and silver, are removed), and may then be refined either by the Pattenson, Parkes, or an electrolytic process. Lead is especially suited for electrolytic refining because of its high electrochemical equivalent and on account of the fact that most of the impurities in the anodes are more electropositive than the lead and do not go into solution electrolytically to foul the electrolyte but stay behind as a metal sponge.

Tanks. In electrolytic lead plants, concrete tanks are replacing wooden ones. Concrete tanks are easily constructed and can be given an impervious lining that will withstand ordinary usage indefinitely provided that the temperature of the circulating electrolyte does not reach the flow point of the asphaltum constituents of the lining. The mixture used in the manufacture of the concrete cells is composed of 1 part cement; 2 parts angular sand; and 3 parts of screened, well-washed,

crushed, siliceous rock 1 in. to 2 in.³³ However, wooden tanks coated with pitch are also used.

The tanks vary in length from 7 to 11 ft. and are 2 ft. 2 in. to 2 ft. 6 in. wide and 3 to 4 ft. deep. They are lined on the inside with asphalt

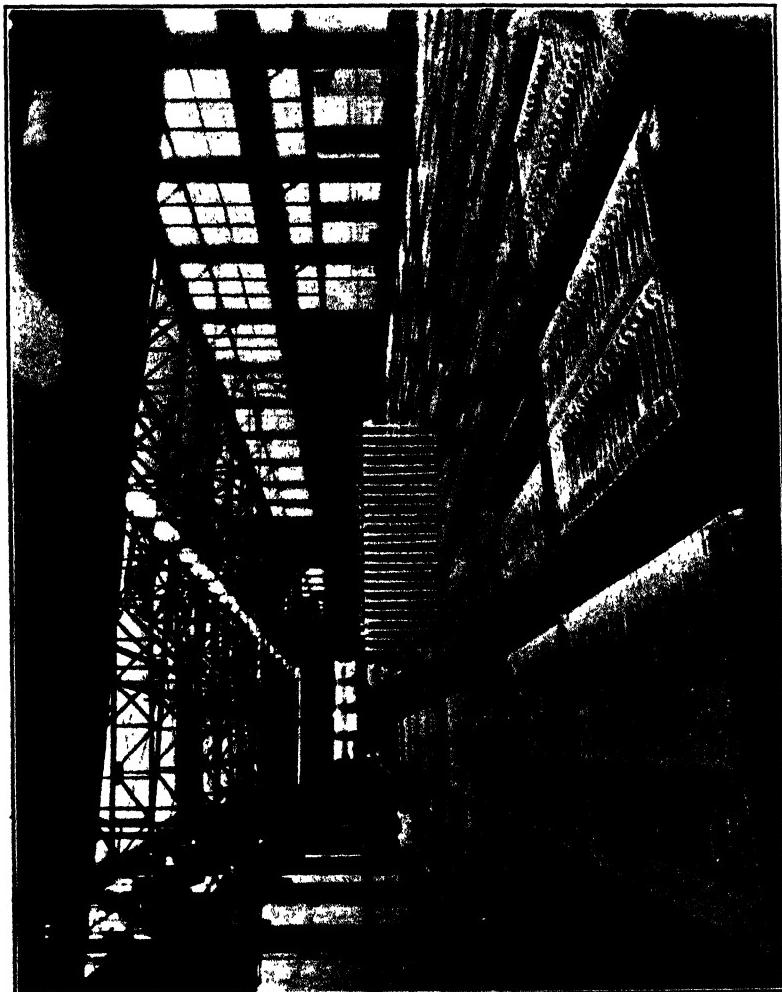


Fig. 64. Tank room of an electrolytic lead refinery. Placing anodes in tank. (Courtesy The Consolidated Mining and Smelting Company of Canada, Ltd.)

having a melting point of 105° C. (220° F.). The asphalt is applied in the melted condition, and care is taken to protect the concrete completely against attack by the acid. It is especially important that the acid electrolyte does not corrode the iron reinforcing, for this will introduce iron into the electrolyte. The whole tank room is designed to avoid

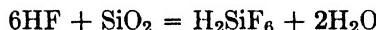
³³ J. J. Finngland, *Trans. Am. Electrochem. Soc.*, **57**, 179 (1930).

contamination by iron. A tank room in a lead refinery is shown in Fig. 64.

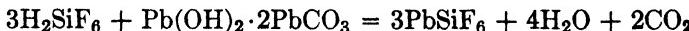
Electrolyte. The electrolyte may be prepared at the refining plant. A mixture of fluorspar, CaF_2 , and sulphuric acid is heated in a retort, which produces hydrofluoric acid, HF, according to the equation:



The hydrofluoric acid is liberated as a gas which is absorbed in water containing finely crushed silica, usually quartz, in suspension. This produces fluosilicic acid as follows:



This results in an aqueous solution of 33 per cent fluosilicic acid.³⁴ This is passed into a box containing granulated lead where lead fluosilicate is produced. This may also be produced by treating the fluosilicic acid with commercial white lead:



The finished electrolyte contains 7 to 10 per cent lead, 3 to 9 per cent free fluosilicic acid, and 5 to 14 per cent combined fluosilicic acid.

Glue or by-product sulphonates called goulac are used as addition agents. A 10 per cent solution of glue is prepared, and a definite amount is added to each tank each day. About 1.5 lb. (680 g.) glue is consumed per ton of lead.³⁵ The glue aids in the production of a strong cathode deposit.

If the anodes contain a large amount of impurities there is a definite depletion of lead in the electrolyte which frequently is taken care of by the introduction of new lead by circulating the electrolyte through tanks containing lead shot wherein the lead is alternately oxidized and then flushed with electrolyte.

Anodes and Cathodes. The anodes are cast in molds and are provided with lugs to support the anodes to make electrical contact with the copper conductors on the tanks. The anodes at the different refineries vary in length from 2 ft. 4 in. to 3 ft.; they are 22 to 26 in. wide and about 1 to 1½ in. thick and weigh from 375 to 450 lb. each.

The anodes contain 98 per cent or more of lead, the remaining percentage being antimony, bismuth, copper, arsenic, tin, and iron. If the lead content is appreciably below 98 per cent, difficulties are experi-

³⁴ J. J. Fingland, *op. cit.*, p. 191.

³⁵ J. J. Fingland, *op. cit.*, p. 192.

enced in electrolysis. Antimony is usually the chief impurity, being present to the extent of 1 per cent or more. Practically all the impurities except copper remain in the antimony slime sponge. Copper, unless present in quantities of 0.04 per cent or less, forms a hard insoluble skin on the surface of the anodes.

The cathode starting sheets are prepared by pouring melted electrolytic lead down an inclined iron table, thus forming a sheet of lead about $\frac{1}{8}$ in. thick and a little larger than the anode. The starting sheets are suspended from bars and are placed in the tanks alternating with the anodes.

Operating Conditions. Each tank contains one more cathode than anode. At present the smallest number of anodes used is 20, and the largest number 28. The electrodes are placed in the tanks with about $1\frac{5}{8}$ in. between electrodes. If the spacing is too close, short circuits may be formed between electrodes with a resultant loss in ampere efficiency. Wider spacing increases the resistance and therefore the energy consumption per pound of lead refined.

The electrolyte is operated at 35 to 40° C. (95 to 104° F.). Too hot a solution softens the asphalt lining; too cold a solution cracks it. By keeping the electrolyte at the proper temperature, the depletion of lead from the electrolyte can be controlled. The temperature is regulated by a copper coil in the first tank through which steam may be passed in winter and cooling water in summer.

The current density at the various refineries varies from 14 to 18 amp. per sq. ft. (1.5 to 1.94 amp. per sq. dm.). This requires 0.34 to 0.6 volt per tank. The voltage is lowest with new anodes, but, as the antimony sponge accumulates on the surface of the anodes, the voltage increases to as much as 0.6 volt or more.

The anodes have a life of about ten days during which time two crops of cathodes are obtained. Only about 65 to 75 per cent of the anode is dissolved; this is in order to maintain a full surface to which the anode sponge may adhere. Whatever impurities fall to the bottom of the tank may cause short circuits and will also produce undesirable chemical reactions in the electrolyte.

The old anodes are removed from the refining tank and are placed in water in a large tank car. The mud is scraped from the anodes, after which they are brushed and rinsed and then sent to the anode kettles to be recast.

Anode Sponge Treatment. The insoluble impurities in the lead anodes consist of antimony, copper, arsenic, bismuth, cadmium, selenium, silver, and gold. The greater part of these impurities remain adhering to the anode in a cellular structure; the antimony content is largely

responsible for this sponge formation. It is important that, during the subsequent filtering and washing of the sponge, the cellular structure is not destroyed.

After the sponge has been filtered and washed it is treated in different ways at various plants. One method is to dry the slimes, after which they are melted in a furnace under reducing conditions to limit oxidation of the metal to a minimum. In this melting process nearly all the arsenic is volatilized and passes off with the gases. Some of the antimony unavoidably forms a lead antimonate slag, $PbO \cdot Sb_2O_3$, but this is avoided as far as possible. This slag also contains silver and is desilverized separately by the addition of coke to give a 10 per cent metal fall which is returned to the melting furnace along with another charge of slimes.

The metal from the first melt is then heated under oxidizing conditions by having a stream of compressed air playing on the surface of the bath. The antimony and arsenic are volatilized as the oxides, Sb_2O_3 and As_2O_3 . These oxides pass off with the fume gas through a settling chamber and then through a Cottrell precipitator. The collected fume averages about 60 per cent antimony, 8 per cent arsenic, 2 per cent lead, and 2 to 20 oz. silver per ton. The last 7 per cent of antimony is not removed as fume but under continued oxidation it forms a lead antimonate slag, which together with litharge, PbO , removes practically all lead from the bath.

After the antimony and lead have been removed, bismuth and copper oxide form a slag on the surface. This scoria is removed as fast as formed in order to expose the liquid surface to the direct oxidizing influence of the air jet. This is continued until a residue of doré metal remains in the furnace.

The bismuth-containing scoria is given a furnace treatment with carbon, producing crude bismuth which is refined electrolytically.

The doré metal contains silver, gold, and palladium. The metal may be parted electrolytically as described under silver refining, or it may be parted by the sulphuric acid process. In either case the gold sludge is melted and cast into anodes and refined by the Wohlwill process which recovers the gold and the small amount of palladium contained in the lead ores treated.

Disposition of the Cathodes. The cathodes are melted and subjected to a final pyrorefining for the removal of any remaining antimony, arsenic, and tin. The molten lead is heated to $538^{\circ} C.$ ($1,000^{\circ} F.$), and compressed air is introduced into the bath so that a lead fountain is formed in the kettle. This mixes the metal and oxidizes the tin, arsenic, and antimony; the oxides collect on the surface of the lead bath, together

with some litharge. This process completely removes the tin and arsenic and reduces the antimony to 0.001 per cent.

BISMUTH

Practically all the bismuth produced in the United States is obtained from the anode mud or sponge at electrolytic lead and tin refineries. The crude bismuth obtained as explained under lead refining is cast into anodes. The anodes contain about 94 per cent bismuth and in addition appreciable amounts of lead, gold, and silver, and some antimony and copper.

The electrolyzing cell is constructed similarly to the Thum cell used in silver refining. The electrolyte contains 5 to 6 g. per liter of bismuth chloride, BiCl_3 , and about 100 g. per liter of hydrochloric acid. The cell is operated at about 55° C . (130° F .). The cathode consists of sheet lead resting on the bottom of the cell. The bismuth is removed from the cathodes periodically.

Little has been published about the electrorefining of bismuth. Mohn³⁶ described a plant used in Mexico. Studies of fluosilicate electrolytes have also been reported.³⁷ The subject of addition agents has been studied by Kern and Jones,³⁸ who found that satisfactory deposits are obtained with an electrolyte containing 70 g. bismuth, 50 g. hydrochloric acid, and 100 g. sodium chloride per liter, or in place of the sodium chloride, 100 g. calcium chloride or 65 g. magnesium chloride per liter. For addition agents 1 g. resorcine, pyrogallol, or benzoic acid per 10 liter of electrolyte is satisfactory.

The deposited bismuth must be free from lead and arsenic, for a considerable portion of the metal is used for medicinals.

IRON

The electrolytic refining of iron has not reached the extensive commercial stage that it appeared it would a decade ago. Electrolytic iron, however, has many useful properties, and it may find more extensive application. By varying operating conditions during deposition the properties of the iron can be varied to a considerable extent. Thus, if the $\text{Fe}^{++}/\text{H}^+$ ion ratio of the bath is high and the electrolysis is conducted at moderate current density and a high temperature, the deposited iron will be ductile. If, on the other hand, the hydrogen-ion concentration is

³⁶ A. Mohn, *Electrochem. Met. Ind.*, **5**, 314 (1907).

³⁷ F. Foerster and E. Schwabe, *Z. Elektrochem.*, **16**, 279 (1910).

³⁸ E. F. Kern and T. R. Jones, *Trans. Am. Electrochem. Soc.*, **57**, 255 (1930).

higher and the temperature of the bath is low, hydrogen will deposit simultaneously with the iron and the deposit will be fine-grained, hard, and brittle.

Electrolytic iron has considerable tensile strength, good resistance to corrosion, and good heat conductivity, and as a result it has been used in France for boiler tubes. The tubes are electroformed by depositing the iron on long cylindrical, rotating cathodes.^{39, 40} In the United States it has in the past found application particularly as a fine powder in the construction of the cores of the loading coils which are introduced at regular intervals to increase the inductance of a telephone circuit.⁴¹ Because of its high purity electrolytic iron has found application in the manufacture of special alloys for the manufacture of electromagnetic instruments.

In 1904 the first attempt was made to produce electrolytic iron on anything approaching a commercial scale.⁴² For this a mixture of ferrous and ammonium sulphates was used. The electrolysis was conducted at 30° C. (86° F.) at a current density of 6 to 10 amp. per sq. ft. (0.65 to 1 amp. per sq. dm.). With some modifications this method has been used in most cases in the United States. The researches up to 1920 have been reviewed by Hughes.⁴³

A process that attained considerable commercial importance was that of the Société "Le Fer," at Grenoble, France; it was used for the formation of tubing.⁴⁴ The electrolyte was made by adding scrap iron to commercial hydrochloric acid; it had a specific gravity of 1.5, contained 24 per cent of iron, and was operated at about 72° C. (162° F.). The anodes consisted of two L-shaped castings for each cell. Part of the anode dissolved electrolytically, but this was not sufficient to maintain the iron content of the electrolyte. The electrolyte was circulated rapidly and before returning to the cell was passed over iron turnings. The cathodes consisted of rotating steel mandrels, about 13 ft. long and varying in thickness from about 3½ to 6¼ in. The larger mandrel rotated at a speed of 180 to 200 r.p.m. The deposit contained about 99.97 per cent iron.

The process of refining iron electrolytically as formerly used by the Westinghouse Electric and Manufacturing Company has been described

³⁹ A. Boucher, English Patent 28,746 (1910); U. S. Patent 1,086,132 (1914); French Patent 458,294 (1912).

⁴⁰ D. Belcher, *Trans. Am. Electrochem. Soc.*, **45**, 455 (1924).

⁴¹ B. Speed and G. W. Elmen, *Trans. Am. Inst. Elec. Engrs.*, **40**, 1321 (1921).

⁴² C. F. Burgess and C. Hambuechen, *Trans. Am. Electrochem. Soc.*, **5**, 201 (1904).

⁴³ W. E. Hughes, *ibid.*, **40**, 185 (1921).

⁴⁴ D. Belcher, *loc. cit.*

by Brace.⁴⁵ The electrolyte is a distilled-water solution of the best grade of technical salts, containing 75 g. per liter $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 150 g. per liter $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 100 g. per liter $(\text{NH}_4)_2\text{SO}_4$. Good deposits are obtained with an iron concentration of 45 to 55 g. per liter and a hydrogen-ion concentration between 1.5×10^{-6} and 0.7×10^{-6} . The acidity is adjusted by the addition of hydrochloric acid or ammonium hydroxide. The electrolysis is operated at 25 to 35° C. (77 to 95° F.), the heat being supplied solely by the passage of the current.

The electrolyte is circulated and filtered in order to avoid contamination of the deposited iron by inclusions of anode sludge.

The anodes are made from Armco iron and are 2 in. by 28 in. by 40 in. long. The cathodes are cut from soft-steel sheets $\frac{1}{16}$ in. by 30 in. by 40 in. long. The cathodes are removed when the deposit is about $\frac{3}{8}$ in. thick. They are washed for 48 hr. in hot water agitated by steam jets, after which the deposited iron is stripped and broken into small pieces for melting. In order to facilitate stripping, the starting sheets are coated with black oxide.

The current density is 10 to 12 amp. per sq. ft. (1.1 to 1.3 amp. per sq. dm.) which requires about 2,000 amp. per cell, with the electrodes connected in multiple, with a maximum of 20 volts.

The tanks are constructed of wood; they are 3 ft. wide, 4 ft. deep, and 6 ft. long and contain 10 anodes and 9 cathodes. All piping in connection with the circulating system is made of lead and stoneware.

Probably no electrolytic iron is produced in the United States at present, although some of the companies that have manufactured it in the past have stocks on hand which they are using for experimental purposes. Up to the second World War electrolytic iron could not compete with "sponge iron" obtained from Norway and Sweden, "Carbonyl iron" obtained from Germany, or Armco iron made in the United States. For telephone loading coils, Permalloy,⁴⁶ a nickel-iron alloy, and Perminvar⁴⁷ have replaced electrolytic iron. If, however, an extremely low sulphur content is required, it is necessary to use electrolytic iron.

ANTIMONY

The largest part of the world's supply of antimony is obtained from China. Pyrometallurgical processes for producing 99 per cent or better

⁴⁵ P. H. Brace, *Trans. Amer. Inst. Elec. Engrs.*, **44**, 549 (1925).

⁴⁶ W. J. Shacketton and I. G. Barber, *Trans. Am. Inst. Elec. Engrs.*, **47**, 429 (1928); W. Fondiller, *Bell Sys. Tech. J.*, **9**, 237 (1930).

⁴⁷ G. W. Elmen, *J. Franklin Inst.*, **206**, 317 (1929).

antimony are simple and involve no special difficulties so that electrorefining has not made much headway.

Various solutions have been tried. In Germany a process was developed using an alkaline sulphantimonite solution. Betts has attempted to use acid solutions of antimony chloride, $SbCl_3$, and ferrous chloride, $FeCl_2$, and also of antimony fluoride, SbF_3 , and ferrous sulphate, $FeSO_4$,⁴⁸ and later⁴⁹ a saturated solution of $SbF_3 \cdot KHF_2$ at a current density of 6.8 amp. per sq. ft. (0.73 amp. per sq. dm.). The electrorefining of antimony, however, has not attained commercial importance in America.

In Germany the Norddeutsche Affinerie produced electrolytic antimony successfully with a solution of sulphuric acid and hydrofluoric acid as electrolyte. In the refining of lead the antimony is removed during the softening of the lead by the Harris process in which the molten bullion is treated with fused sodium hydroxide and a little sodium nitrate. The antimony is removed as sodium antimonate. It is reduced to raw antimony in a small reverberatory furnace and cast into anodes.

The electrolyte contains 20 g. per liter of hydrofluoric acid and about 250 g. per liter of sulphuric acid. The antimony is deposited on starting sheets of copper with a purity of 99.8 per cent. A current density of 9.3 amp. per sq. ft. (1 amp. per sq. dm.) is used.

TIN

Tin was refined electrolytically in the United States for about 6 years beginning in 1916. During the first World War impure ores were obtained from Bolivia and electrorefining was necessary in order to obtain a good grade of tin. Electrolytic refining of tin produces a metal of 99.90 per cent purity or better. The main electrorefining operations were conducted at the Perth Amboy plant of the American Smelting and Refining Company, and have been described by Stack.⁵⁰ The tanks and equipment were very similar to those of a copper refinery.

Electrolytes. Several different types of electrolytes for tin refining have been used and found successful to some extent. These have been described by Stack⁵⁰ and Mantell.⁵¹

The fluosilicic bath contained about 20 per cent fluosilicic acid, H_2SiF_6 , 0.1 per cent sulphuric acid, and 6 per cent stannous tin. Glue

⁴⁸ A. G. Betts, *Trans. Am. Electrochem. Soc.*, **8**, 187 (1905).

⁴⁹ A. G. Betts, *ibid.*, **28**, 325 (1915).

⁵⁰ J. R. Stack, *ibid.*, **45**, 441 (1924).

⁵¹ C. L. Mantell, *Tin*, Chemical Catalog Co., New York, 1929; *Trans. Am. Electrochem. Soc.*, **45**, 431 (1924).

and cresylic acid were used as addition agents. This bath gave well-adhering crystalline deposits. This bath was later modified to contain a larger amount of sulphuric acid, so that the analysis was approximately 8 per cent sulphuric acid, 5 per cent fluosilicic acid, and 3 per cent stannous tin, with the same addition agents. The fluosilicic acid was used to prevent the formation of basic salts of tin. The conductivity of this bath was found to be especially good. In 1920 the fluosilicic acid was replaced by a more efficient and cheaper substitute in the form of sulphonic acid of an aromatic hydrocarbon such as benzol, phenol, cresol, or toluene. The composition then was 8 per cent sulphuric acid, 4 per cent cresol-phenol sulphonic acid, and 3 per cent stannous tin. The use of glue and cresylic acid as addition agents is very important in obtaining smooth and dense deposits.⁵²

Operating Conditions. The temperature of the electrolyte is an important factor in obtaining uniform anode corrosion and soft slimes adhering to the anode. The most desirable operating temperature is 35° C. (95° F.). The current density under normal conditions with 95 per cent tin anodes was 10 amp. per sq. ft. (1.1 amp. per sq. dm.) at 0.35 volt per tank.

The anodes remained in the tanks for 21 days, during which time three crops of cathodes were pulled.

The electrolyte was circulated at the rate of 4 to 5 gal. per min. If treeing occurred at the cathodes a small amount of hydrochloric acid was added to the electrolyte.

Slimes Treatment. The slimes formed remained for the most part on the anodes, so that it was necessary to leave about 25 per cent scrap for a continuous surface on which the slimes might adhere. The slimes contained about 0.12 oz. per ton gold, 130 oz. per ton silver, 20 per cent lead, 5 per cent copper, 3 per cent arsenic, 5 per cent antimony, 20 per cent bismuth, and 30 per cent tin. The slimes were largely finely divided metallic particles.

In the fusion method the slimes were fused in a cupel furnace under oxidizing conditions under a flux of sodium hydroxide or sodium carbonate for the removal of tin, arsenic, and antimony. Repeated fusions were made by intermittently granulating the crude metal, mixing with soda, and recharging. The soda slag containing the arsenic, part of the antimony, and most of the tin was resmelted, and the resultant metal refined electrolytically. The detinned bullion was shipped to the electrolytic lead refinery for recovery of the bismuth.

In another method the slimes were reduced to metal and cast into anodes, then electrolyzed in a diaphragm cell in an 18 per cent hydro-

⁵² F. C. Mathers, *Trans. Am. Electrochem. Soc.*, 45, 449 (1924).

chloric acid solution with a current density of 25 amp. per sq. ft. (2.8 amp. per sq. dm.) at 40° C. (100° F.). The gold, silver, lead, and arsenic did not dissolve; 35 per cent of the copper, 45 per cent of the antimony, 90 per cent of the tin, and 90 per cent of the bismuth went into solution. Electrolysis was stopped when the anolyte became saturated with these metallic salts. The bismuth in the solution was cemented out on impure tin, refined by fusion with soda and sulphur, and sent to the lead refinery for further electrolytic refining. The anode slimes, high in lead, were smelted and desilverized.

SOLDER

Formerly all solder was made by melting together virgin lead and tin in the desired proportions; today the base of most solders comes from scrap or secondary materials such as solder-bearing scrap, drosses, and residues. Refined solder may be obtained by furnace processes which remove the baser metals but have no effect on gold and silver; these noble metals may be present in a large proportion of the tin-lead material available.

An electrolytic process has been described⁵³ in which both base impurities and precious metals are removed in one operation, and thousands of tons of solder have been produced by this method.

The impure solder is melted and given a partial purification; this consists of stirring sulphur into the cooled liquid metal, which reduces the copper content below 0.5 per cent. This may or may not be followed by further purification to reduce the arsenic and antimony content, depending upon the amounts present. If too many alloying metals are present, the major part of the tin is combined chemically in such compounds as Cu₂Sn, SbSn, AsSn, Fe₃Sn, and FeSn₂, and in addition there will be formed other compounds such as Cu₃Sb, FeSb₂, and others. These metallic compounds act as inert in the anode and therefore stay behind while the lead and uncombined tin go into solution electrolytically. Such anodes become passive and completely insoluble after several hours when the lead and free tin have gone into solution and a structure of the inert remains behind. It is therefore necessary to remove these impurities to such an extent as to produce a residual anode slime that will adhere to the anode without producing passive anodes. The following composition is typical of anodes in use: lead, 62 per cent; tin, 35; antimony, 2; copper, 0.05; arsenic, 0.25; iron, nil; gold, 0.05 oz. per ton; and silver, 30 oz. per ton.

⁵³ R. P. E. Hermsdorf and Max Heberlein, *Trans. Am. Inst. Mining Met. Engrs.*, 121, 289 (1936).

After the preliminary treatment the metal is cast into anodes which weigh 350 to 400 lb. each. The cathode starting sheets are made by pouring molten electrolytic solder from a trough over an inclined polished steel plate having the exact dimensions and shape desired.

The electrolyte consists of a solution of lead fluosilicate, tin fluosilicate, and free hydrofluosilicic acid. The composition is approximately: Pb, 30 g. per liter; Sn, 40; free H_2SiF_6 , 65; total acid, 140. In regular operation the electrolyte is continually circulated through the electrolysis tanks, entering at the top and leaving at the bottom. The electrolyte flows to a central tank equipped with steam coils where it is heated to 40° C. (105° F.), the temperature maintained in the plating tanks.

During electrolysis small amounts of iron, nickel, and zinc, which stand above lead and tin in the electromotive series, are continually going into solution and would eventually foul the electrolyte. To keep these impurities down to working limits the solution is circulated through a tank containing solder shot, which checks the accumulation of these impurities. This tank is placed between the electrolysis and heating tanks.

Each electrolysis tank holds 31 anodes and 32 cathodes. The tanks are made of concrete lined with pitch and mastic. The operating voltage is about 0.34 volt between electrodes; the current density is 15 amp. per sq. ft. of cathode area.

Spectrographic analysis shows that the following metals are present in the cathode in quantities under 0.001 per cent: copper, silver, bismuth, iron, nickel, magnesium, silicon, and calcium; undetected are zinc, aluminum, phosphorus, arsenic, gold, barium, cadmium, chromium, gallium, germanium, mercury, lithium, manganese, molybdenum, and sodium. The antimony content averages around 0.02 per cent, but this is lower than is found in most solders, and it may be necessary to add antimony to meet the specifications of the buyer.

The lead-tin ratio of the cathode is not definitely controlled but is allowed to wander with the input of anodes, and is then blended with virgin tin or lead to meet the specifications demanded.

ZINC

Zinc obtained from distillation furnaces contains 96 to 98.5 per cent zinc; the impurities are lead, iron, cadmium, copper, antimony, arsenic, and silicon. It may be further refined by liquation, redistillation, or electrolysis. Electrolytic refining of crude zinc produces a very pure product. Electrolytic refining of zinc has been tried in the past, but the process is far more expensive than either of the other methods and

is not practiced today on a large scale. Electrolytic refining has been used successfully for recovery of zinc from zinc-base die-castings.

During the first World War the demand for pure zinc for cartridge brass stimulated research which led to the present electrolytic method for the reduction of zinc ores. This, however, is an electrowinning process and is therefore discussed in the following chapter.

ALUMINUM

It is not possible to electrorefine aluminum using an aqueous solution. On account of their expensive nature and high electrical resistivity, organic solvents for aluminum have not proved practicable. It is therefore necessary to use a fused electrolyte which in present practice consists of a mixture of cryolite, AlF_3 , barium fluoride, BaF_2 , and alumina, Al_2O_3 . The discussion of the refining of aluminum will therefore be deferred to a later chapter in connection with the production of aluminum, after the nature of fused electrolytes has been discussed.

CHAPTER VIII

ELECTROMETALLURGY

THE ELECTROLYSIS OF AQUEOUS SOLUTIONS

In electrometallurgy the metal to be recovered is first obtained as an electrolyte from which it is precipitated electrolytically. Two general methods are in use: (a) The prepared ore is leached in a suitable solution, and the solution, containing the major portion of the metal, is then subjected to electrolysis, producing a relatively pure metal. This is the process discussed in the present chapter. (b) A suitable compound of the metal is fused, and the fusion is then subjected to electrolysis, producing the metal in refined form. This process is discussed in the following chapter.

In a number of applications, electrometallurgy competes successfully with pyrometallurgy. In fact, in a number of cases to be discussed in the next chapter, electrometallurgy finds no competition whatever from pyrometallurgical processes. In others, electrochemical processes find special application for certain grade of ores, or in certain communities.

The term "electrowinning" is also used in place of "electrometallurgy," and if aqueous solutions are used, as in copper and zinc, the term "electrohydrometallurgy" is also applied.

COPPER

The electrowinning of copper is applied especially to low-grade ores, the copper content being between 1 and 2 per cent. For such ores the production costs are lower than in pyrometallurgical processes, although the plants employing those processes use higher-grade copper ores.

In the electrometallurgical process, the ores are leached with a suitable solution which removes part of the copper. Generally the copper content of the leached ore is less than 0.2 per cent. This enriched solution becomes the electrolyte in the electrolytic plant, where, with the use of insoluble anodes, a portion of the copper is plated out as electrolytic copper. The solution is then returned to the leaching tanks to leach fresh ores, so that the process is a cyclic one.

The processes for the electrometallurgy of copper described in this chapter are largely those used at the Chile Copper Company,¹ Chuquicamata, Chile; the Inspiration Consolidated Copper Company,² Inspiration, Arizona; the New Cornelia mines of the Calumet and Arizona Mining Company,^{3, 4, 5} Ajo, Arizona, not now in operation; and to some extent in the experimental work at the Bagdad Copper Corporation,⁶ Hillside, Arizona.

Nature of the Ore. At New Cornelia the oxidized capping extends down to a horizontal plane corresponding to the water level. The predominating copper mineral in this zone is malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; the chief sulphide minerals below this zone are chalcopyrite, CuFeS_2 , and bornite, Cu_5FeS_4 , with small amounts of chalcocite, Cu_2S . The analysis of the ore is shown in (a), Table XXIII.

TABLE XXIII
ANALYSES OF COPPER ORES USED FOR LEACHING

Main Copper-Bearing Minerals	(a)	(b)	
	Copper	Per Cent	Per Cent
Iron	1.13	4.65	1.41
SiO_2	46.40	64.40	66.10
Al_2O_3	15.33	15.33	17.70
CaO	0.55	0.55	0.20
MgO	1.26	1.26	0.68
Na_2O	1.80	1.80	1.08
K_2O	3.45	3.45	5.78
H_2O	1.05	1.05	0.70
Difference	6.38	6.38	4.77

(a) The New Cornelia Mines, Ajo, Ariz., G. A. Bell, *Information Circ.* 6303, p. 3, U. S. Bur. Mines, July 1930.

(b) Chuquicamata, Chile, C. W. Eichrodt, *Trans. Am. Inst. Mining Met. Eng.*, 1930, p. 186.

¹ C. W. Eichrodt, *Trans. Am. Inst. Mining Engrs.*, 1930, p. 186.

² H. W. Aldrich and W. G. Scott, *Eng. Mining J.*, 128, 612 (1929).

³ G. A. Bell, *Information Circ.* 6303, U. S. Bur. Mines, July, 1930.

⁴ H. A. Tobelmann and J. A. Potter, *Trans. Am. Inst. Mining Met. Engrs.*, 60, 22 (1919).

⁵ A. W. Allen, *Eng. Mining J. Press*, 113, 1003, 1051; 114, 184 (1922).

⁶ C. T. Baroch, *Trans. Am. Electrochem. Soc.*, 57, 205 (1930).

At Chuquicamata the copper ores treated lie between the leached zone, or capping, and the zone containing the mixed oxides and sulphides. The principal copper minerals are chalcanthite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; brochantite, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$; and atacamite, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$. The analysis of an unweighted composite of the ore for one year is shown in (b), Table XXIII.

At the Bagdad property the ore minerals are principally chalcopyrite, CuFeS_2 , and chalcocite, Cu_2S .

Preparation of the Ore. The only treatment the ore receives after mining, preparatory to leaching, is crushing, grinding, and screening, except that in one instance the ore is concentrated and roasted. Size that will pass through a $\frac{1}{4}$ -in. opening is generally satisfactory, but the actual size varies with the nature of the ore. At Inspiration the screen opening has varied from $\frac{1}{2}$ by $\frac{7}{8}$ in. to $\frac{1}{4}$ by $\frac{1}{2}$ in. If the particles are large, leaching is slow and less complete; but if the grinding is to less than $\frac{1}{4}$ in. much fines is produced, which, in certain ores, becomes slimy in the leaching tanks and thus makes for poor and incomplete leaching.

In the experimental plant of the Bagdad Copper Corporation the ores are concentrated by flotation, giving a concentrate containing between 30 and 35 per cent copper. The concentrates are roasted, the object being to put the copper in the form of cupric oxide, CuO , which is very soluble in the leaching acid, and to put the iron in the form of least solubility, ferric oxide, Fe_2O_3 . In practice, however, some copper remains as cuprous oxide, Cu_2O , which does not dissolve as readily.

The Leaching Tanks. The tanks or vats in which the ore is leached are made of reinforced concrete, lined either with lead or with mastic. At New Cornelia, 12 tanks are used, each tank being 88 ft. square and 17 ft. 4 in. deep. At Inspiration the 13 tanks are each 175 ft. by $67\frac{1}{2}$ ft. by 18 ft. deep. All the above tanks are lead lined. The lining is protected from the ore by 2-in. planks, supported on upright pieces of timber. Each tank has a false bottom or filter-floor made of 2-in. planks supported on joists, which at one plant are 5 by 12 in. placed on edge. The filter boards have $\frac{3}{8}$ -in. holes drilled through them, 15 to 36 per sq. ft. of surface; the holes are countersunk from the under side. At the plant of the Chile Copper Company, the tanks are 150 by 110 ft., six being 17 ft. 5 in. deep and seven $19\frac{1}{2}$ ft. deep. The tanks have a mastic lining 4 in. thick, also reinforced. The present type of mastic lining gives evidence of a life of 20 years with little repair. The filter-floor is constructed differently from the others described. Joists, 6 by 6 in., of Oregon pine are placed on the tank bottom, 10 in. apart. Planks 2 by 6 in. are laid on top of the joists, spaced 3 in. apart. These planks are covered with a layer of cocoa matting, and on top of the matting is

placed a layer of 2-in. planks at right angles to the first layer. The upper planks are spaced $\frac{3}{8}$ in. apart.

All the tanks have one or more openings in the floor for introducing the solution and for draining the tanks.

The Leaching Process. The ground ore is charged into the tanks by means of conveyor belts and trippers running on a movable spreader bridge that spans the leaching tanks. The amount of ore charged varies

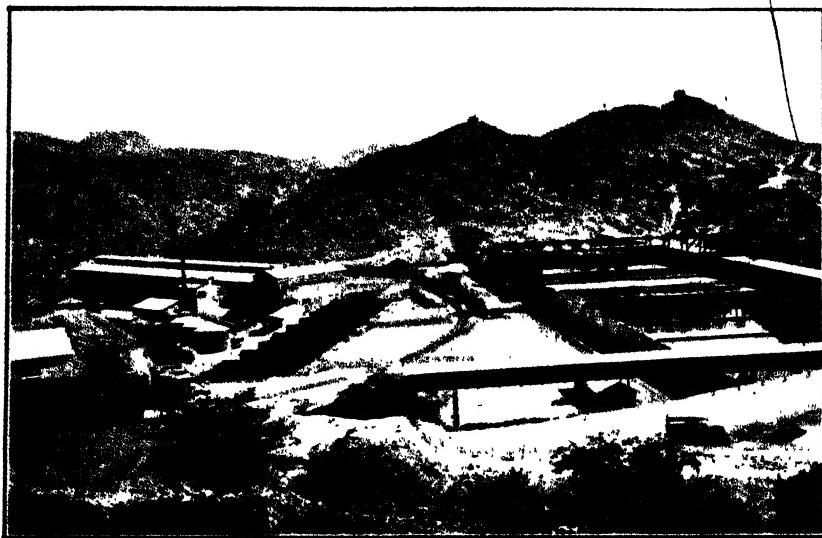


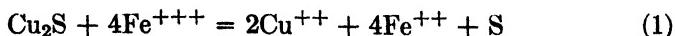
FIG. 65. General view of a copper ore leaching plant. (*Courtesy Inspiration Consolidated Copper Company.*)

with the size of the tank and ranges generally from 5,000 to 10,000 tons per tank. A general view of a copper ore leaching plant is shown in Figs. 65 and 66. While the ore is being charged, the leaching solution may be introduced into the tank from the bottom so that the ore is covered with solution throughout the charging, or the tanks may be charged dry and the solution then pumped in from the bottom.

For oxidized ores, in which the copper is present as oxide, hydroxide, carbonate, or basic sulphate, dilute sulphuric acid is commonly used as the leaching agent. This may be spent electrolyte from the electrolytic plant where part of the copper has been removed and the acid has been regenerated. The leaching solution may also be, in part, the first wash water after the acid leaching has been completed.

If the ore contains the copper as sulphide, sulphuric acid alone will not leach the ore. At the New Cornelia mines the sulphide ore was leached with a sulphuric acid solution containing on an average 7.5 g.

per liter of ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$. The reaction may be represented by



giving an electrolyte containing copper sulphate and ferric and ferrous sulphates. Later, few sulphide ores were leached and no ferric sulphate



FIG. 66. General view, mine surface plant and leaching plant. International smelter in background. (*Courtesy Inspiration Consolidated Copper Company.*)

was used; on the contrary, any ferric sulphate in the solution was reduced in towers by sulphur dioxide in order to increase the power efficiency in the tank house.

At Inspiration, the ores in 8 tanks out of the 13 are receiving the acid treatment and are connected in series with regard to the flow of the solution. These tanks are all charged with ore on consecutive days so that the tank at one end has just received the acid leach while the one on the other end has been leaching eight days and is ready to be drained. The spent electrolyte (i.e., the regenerated leaching solution) with the addition of some new acid is delivered to the oldest ore under acid contact. It percolates up through the ore, overflows through a launder, and goes to the suction of the pump serving the next tank. This pump is a vertical screw type lead pump, and there is one for each tank. The pump introduces the acid under the filter bottom of

the next tank. The solution flows from tank to tank, constantly being reduced in solvent strength and increased in copper content until it emerges from the newest ore, after which it flows back to the tank house.

At Chuquicamata, the tanks are not connected in series. The first solution on the ore, called the "treatment" solution, is introduced from the bottom of the vat and percolates upward until the ore is covered. This solution is relatively low in copper and high in free acid, and is the first wash obtained after the acid treatment. After a soaking period, the solution, which has been enriched in copper with an accompanying conversion of the free acid to copper sulphate, is withdrawn from the bottom and fresh leaching solution is added to the top of the tank at such a rate as to keep the ore covered. This second solution is spent electrolyte and is also relatively low in copper and high in free acid. Generally three batches of solution are added, one of treatment solution and two of spent electrolyte. Each is allowed to soak the ore for a period of time and is then drained off and replaced by another solution. The drained solutions are called "strong" solutions; they are mixed with strong solutions from other vats and sent to the dechloridizing plant and then to the electrolysis cells for removal of part of their copper.

The strong solution averages about 35 g. per liter of copper and 48 g. per liter of sulphuric acid.

At the plant of the Inspiration Consolidated Copper Company at Inspiration, Arizona, the ore is a mixture of copper oxide and sulphide. The usual sulphuric acid leaching solution has little effect on the chalcocite, Cu_2S , which contains a large part of the available copper. The leaching solution therefore contains ferric sulphate, $Fe_2(SO_4)_3$, at an average concentration of about 7.5 g. per liter. The ferric sulphate dissolves the sulphide copper, but it is also a detriment to electrolytic precipitation efficiency in the tank house.

After the soaking and leaching are completed it is necessary to wash the ore to remove the strong solution in the pores. This is a very important phase of the operation. Aldrich and Scott⁷ point out that a tank of 9,000 dry tons of ore will carry 11.67 per cent or 1,050 tons of moisture when discharged as tailings. The final solution drain averages 20.25 g. per liter of copper, so that the amount of copper to be washed out is 42,525 lb. per tank, which represents over 29 per cent of the daily production.

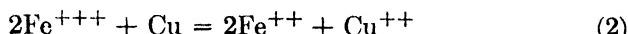
At Inspiration, three days are taken for washing, using ten washes altogether. The first four washes go to the regular solution system,

⁷ H. W. Aldrich and W. G. Scott, *Eng. Mining J.*, 128, 612 (1929).

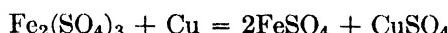
the fifth wash becomes the fourth wash on the next tank to be washed, and so on. The last five washes then go to a series of iron launders where the copper is precipitated by cementation.

At Chuquicamata the first wash is added to the top of the tank while the last leach solution is being withdrawn, the ore being covered all the time, a process amounting to nearly a piston displacement of solutions. The first tank full of wash solution is sent to a tank filled with fresh ore and becomes the "treatment" solution mentioned earlier in the discussion. The final discarded solution is freed of copper by cementation or may be sent to the tank house to be "plated down" electrolytically and then finally stripped of copper at the dechloridizing plant.

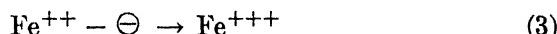
Reduction of Ferric Iron. Ferric iron is objectionable in the electrolyte for it dissolves copper at the cathodes and reduces the tank-house efficiency correspondingly. The reaction at the cathode is



or



Addicks⁸ reported that with a copper sulphate solution containing 0.75 per cent Fe^{+++} , no copper was deposited at the cathode at 51° C. (123° F.) with a current density of 13 amp. per sq. ft. (1.5 amp. per sq. dm.). Ferrous iron is oxidized to the ferric at the anode if insoluble anodes are used, as in copper extraction. The potential required for the reaction



is lower than that required for the reaction



so that, with a moderate Fe^{++} concentration and a well-circulated electrolyte, the reaction represented by equation 4 may not take place at all.⁹ The ferric iron may then find its way to the cathode where the reaction represented by equation 2 will take place. At Inspiration, however, tanks are run at times with over 0.8 per cent ferric iron with a cathode efficiency of 69.7 per cent. In the practical electrometallurgy of copper, ferrous iron is considered harmless,¹⁰ and sometimes no attempt is made to remove the iron but instead it is reduced to the ferrous state.

⁸ L. Addicks, *Trans. Am. Electrochem. Soc.*, **28**, 88 (1915).

⁹ A. J. Allmand and H. J. T. Ellingham, *Applied Electrochemistry*, second edition, pp. 284-285, Edward Arnold and Company, London, 1924.

¹⁰ A. W. Allen, *Eng. Mining J. Press*, **113**, 1051 (1922).

Even then, not all the iron is reduced, for some ferric iron is desirable, as it aids in the solution of the copper during the leaching process. Some plants, however, like the Andes Copper Mining Company, Potrerillos, Chile, do remove iron from the solution by precipitating ferric iron along

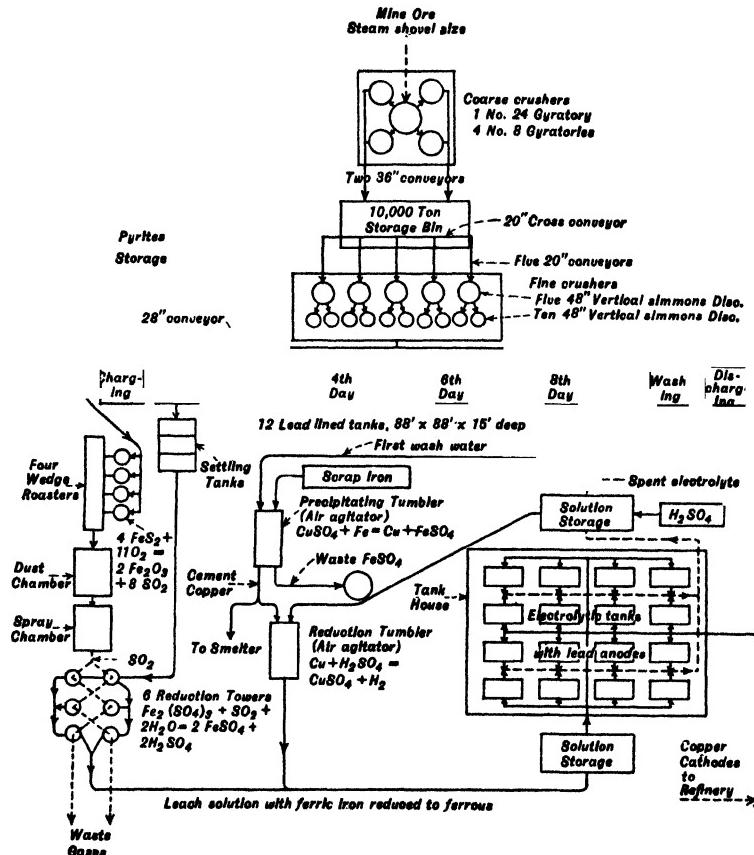
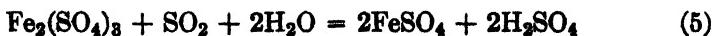


FIG. 67. Flow sheet for the electrometallurgy of copper at the Calumet and Arizona Mining Company.

with other impurities by the addition of lime to the nearly neutral solution off the leach.

Some copper ores contain iron in such small quantities that no reduction is needed. At the New Cornelia Mines of the Calumet and Arizona Mining Company, Ajo, Arizona, the ferric iron is reduced by sulphur dioxide. The reaction may be represented by



The generation of sulphuric acid in the towers is also desirable, for the acid can be used in the leaching solution. The sulphur dioxide is produced from pyrites, FeS_2 , in Wedge roasters. The gas passes through dust and spray chambers and then to the reaction towers where it meets the leach solution and reduces the ferric iron below 0.4 per cent.

Last traces of ferric iron or even all of it can be removed by passing the solution over cement copper. This process is undesirable, for no



FIG. 68. Slimes treatment plant, copper electrometallurgy. (*Courtesy Inspiration Consolidated Copper Company.*)

sulphuric acid is produced as in equation 5, the cost of producing cement copper is relatively high, and the dissolved copper must be reprecipitated electrolytically. Figure 67 shows a flow sheet which includes the reduction of the iron; Fig. 68 shows a slimes treatment plant.

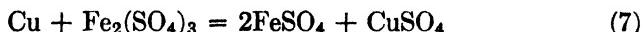
The Calumet and Arizona Mining Company is the only large plant that finds it necessary to use special equipment to reduce the iron. At the Chile Copper Company the iron is reduced in the dechloridizing plant and will be mentioned in the discussion of the removal of chlorine. The Inspiration Consolidated Copper Company, Inspiration, Arizona, permits ferric sulphate, purposely, to dissolve the sulphide copper, but suffers a corresponding decrease in tank-house efficiency. At the experimental plant of the Bagdad Copper Corporation, Hillside, Arizona,

where also a sulphide ore is used, the ore is concentrated and then roasted, which oxidizes the copper and thus makes it easily soluble in dilute sulphuric acid and also oxidizes the iron and thus makes it very poorly soluble in the acid.

Removal of Chlorine. The Chile Copper Company has a dechloridizing plant which was designed primarily to remove the chlorine from the strong solution before it passed to the electrolysis cells. The functions of this plant have been extended to decopperizing the solutions to be discarded and reducing ferric iron in the strong solution.

Chlorine, especially when present in amounts greater than 0.5 g. per liter, destroys the lead peroxide film covering the surface of the Chilex anode, and it is this film that is the important feature of that anode.¹¹ Chlorine is precipitated to some extent on the surface of the cathode as cuprous chloride, which is objectionable in the wirebar furnace. Chlorine also promotes the growth of needles and nodules on the surface of the cathode, creating probabilities of short circuits.

As the strong solution enters the dechloridizing plant a small portion is by-passed to an agitator tank where it is used to emulsify washed cement copper. The emulsion formed is fed back to the solution of strong electrolyte and then passes through another agitator where chlorine is removed and the iron is reduced:



The cuprous chloride, Cu_2Cl_2 , is but slightly soluble in the solution and settles out in settling tanks.

The Electrolytic Plant or Tank House. The leach solution from the tanks, after having its ferric iron reduced to the ferrous state and the chlorine removed (but both these steps are omitted in some plants), is sent to the tank house to have part of the copper removed electrolytically. Figure 69 shows the interior of a tank house.

The copper can also be removed by cementation on iron, but Baroch¹² has produced figures to show that the cost of precipitating copper electrolytically is only about 55 per cent as great as the cost by iron precipitation per unit of copper produced.

The electrolytic plant is very similar to a copper refinery except that insoluble anodes are used. The anodes are commonly rolled antimonial lead, but the Chile Copper Company uses a special anode called Chilex

¹¹ Personal communication from C. W. Eichrodt, Nichols Copper Company, Laurel Hill, New York.

¹² C. T. Baroch, *loc. cit.*, p. 221.



FIG. 69. Tank-house interior, copper electrometallurgy plant. (*Courtesy Inspiration Consolidated Copper Company.*)

which is an alloy of copper, silicon, iron, and lead with small amounts of other metals.¹³ The use of insoluble anodes involves a higher energy consumption for deposition of the copper than is required in electrorefining where copper anodes are used. Bray¹⁴ states that roughly ten times as much energy is consumed with insoluble anodes as in the multiple system of refining as indicated below:

Insoluble electrodes	0.8 lb. of Cu per kw-hr.
Multiple system of refining	8.0 lb. of Cu per kw-hr.
Series system of refining	14.0 lb. of Cu per kw-hr.

Starting sheets are made by depositing copper on smooth sheets of rolled copper as in the copper refineries.

The electrolytes contain about 24 to 36 g. per liter of copper and 20 to 48 g. per liter of sulphuric acid. The total iron may be as much as 20 g. per liter, but the ferric iron is well under 1 g. per liter, except where ferric sulphate is produced purposely by the oxidation of ferrous sulphate, when ferric iron may be as high as 6 g. per liter. Copper deposition efficiencies are at their best when the electrolyte contains more than 20 g. per liter of copper, but a solution of 60 g. per liter of copper and 10 g. per liter of acid does not contain sufficient acid for good conductivity.¹⁵ The composition of an electrolyte¹⁶ is given in Table XXIV.

TABLE XXIV
ANALYSIS OF ELECTROLYTE FROM COPPER LEACH

	Per Cent		Per Cent
Combined H ₂ SO ₄	14.23	MgO	0.76
Free H ₂ SO ₄	1.69	MnO	0.06
Total iron	1.44	P ₂ O ₅	0.23
Ferric iron	0.08	Zinc	Trace
Copper	2.64	Arsenic	0.00
Chlorine	0.012	Antimony	0.00
Al ₂ O ₃	1.51	Tellurium	Trace
CaO	0.09		

The spent electrolyte leaving the cell has the copper content reduced considerably while the acid content is increased. At the various plants the copper content ranges from 14 to 24 g. per liter and the sulphuric acid from 24 to 80 g. per liter.

¹³ C. W. Eichrodt, *Trans. Am. Electrochem. Soc.*, **45**, 390 (1924).

¹⁴ J. L. Bray, *The Principles of Metallurgy*, p. 190, Ginn and Company, New York, 1929.

¹⁵ C. T. Baroch, *op. cit.*, p. 226.

¹⁶ G. A. Bell, *op. cit.*, p. 19.

Current densities used range from 5.5 to 12 amp. per sq. ft. (0.6 to 1.3 amp. per sq. dm.), although densities up to 20 amp. per sq. ft. (2.1 amp. per sq. dm.) have been used successfully.¹⁷ Current efficiencies as high as 90 per cent have been attained, but where ferrous sulphate is used, the current efficiency is about 65 per cent.

Analysis of some cathode copper is given in Table XXV.

TABLE XXV
ANALYSIS OF CATHODE COPPER

	(a) Per Cent	(b) Per Cent		(a) Per Cent	(b) Per Cent
Copper	99.980	99.201	Antimony	0.0003	0.000
Sulphuric acid	0.312	Bismuth	0.0006
Sulphur	0.0009	Lead	0.0007
Oxygen	0.010	Iron	0.0010
Chlorine	0.157	Insoluble	0.0095	0.125
Arsenic	0.0005	0.000	$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	0.113

(a) C. T. Baroch, *loc. cit.*, p. 227.

(b) G. A. Bell, *loc. cit.*, p. 18.

ZINC

Before the first World War practically all zinc ores were treated by distillation in retorts. Electrometallurgy had not made much progress, for the process was more expensive than pyrometallurgy and the market for the pure zinc produced was very limited. However, small quantities of impurities in brass greatly impair its malleability so that the demand for very pure brass for cartridge cases stimulated research that led to the present method of electrometallurgy. This method also opened the way for the use of low-grade zinc ores that could not readily be used in pyrometallurgical processes.

The electrolytic zinc process offers the following advantages over the retort method: It permits the treatment of low-grade zinc which cannot be treated by smelting; it produces a higher grade of metal; it allows a higher extraction of zinc; and it recovers a number of other metals in the ore which are ordinarily lost in the smelting operation.

After the first world war, electrometallurgy of zinc gained steady favor, and now it accounts for about 25 per cent of the total zinc production.

The ore is ground and usually concentrated, and then roasted to convert the sulphide, ZnS , to the oxide and sulphate, ZnO and ZnSO_4 . The roasted ore is leached with a dilute sulphuric acid solution; the solution is purified and then electrolyzed in tanks with insoluble anodes.

¹⁷ C. T. Baroch, *op. cit.*, p. 226.

Nature of the Ore. The chief commercial ores of zinc are the sulphide ore, sphalerite, carrying zinc blende, ZnS ; calamine, $(ZnOH)_2SiO_3$; and smithsonite, $ZnCO_3$. The last two are generally found associated and pass under the name of calamine. The average zinc content of the ores as mined is generally under 5 per cent. Many ores are very complex, which introduces difficulties in the metallurgical processes.

Preparation of the Ore. The actual treatment of the ore differs somewhat at the different plants, but the method used at the Sullivan mine of the Consolidated Mining and Smelting Company of Canada, Ltd.,¹⁸ at Trail, British Columbia, may be taken as fairly representative. Ore from the mine is fed to a large jaw crusher where it is reduced to 8-in. size, then to gyratory crushers which reduce it further to $2\frac{1}{2}$ -in. size. The crushed ore then goes to the fine crushing plant where it is reduced to $\frac{5}{8}$ -in. size in roll crushers. It is necessary to grind Sullivan ore to a finer state than is usual in other milling practice. The ore is further reduced in two stages in Hardinge ball mills so that 85 per cent will pass a 200-mesh screen. A great share of the zinc ore produced at other mines, however, is crushed to only 48 mesh.

Practically all zinc ores must be concentrated; only a few ores have a sufficiently high zinc content that concentration is not necessary. Therefore, the ore is concentrated by flotation, which produces a zinc concentrate of the following average analysis: Zn, 51.1 per cent; Pb, 3.5; Fe, 11.4; S, 32.8; Cu, 0.14; SiO_2 , 0.6; Mn, 0.52; CaO, 0.2; Cd, 0.16; Ag, 2.2 oz. per ton; moisture, 9 to 10 per cent.

The concentrated ore is roasted in order to render the zinc soluble in the acid leaching solution. The zinc sulphide is converted to zinc oxide and zinc sulphate, both of which are soluble in the acid. The roasting of the ore is one of the most difficult processes in the line. If the roasting temperature is too high when complex ores containing iron and lead are roasted, or if the lead- and iron-bearing particles are in intimate contact, the lead forms a coat over the ore particles and thus prevents further oxidation. Iron combines with the zinc to form zinc ferrite, $ZnO \cdot Fe_2O_3$. If the iron content is 5 per cent or less all the iron will be thus combined. In roasting the complex Sullivan ore, which is a highly ferruginous marmatite (approximately $FeS \cdot 7ZnS$), all the iron so combined forms ferrite under normal roasting conditions. The zinc ferrite is not soluble in the leaching solution unless the acid concentration is fairly high.

For distillation processes ores are roasted so that all the zinc is oxidized

¹⁸ B. A. Stimmel, W. H. Hannay, and K. D. McBean, *Trans. Mining Met. Engrs.*, **121**, 540 (1936); J. B. Hutt, *Eng. Mining J.*, **139**, 42 (1938); W. M. Archibald and associates, *Trans. Can. Inst. Mining Met.*, **27**, 306 (1924).

to zinc oxide. For leaching purposes, however, it is desirable to convert some of the sulphide to zinc sulphate so that in the electrolysis tanks the corresponding amount of sulphuric acid will be formed to replace that lost in the process, such as that in solution spills and that lost in the residue. Since zinc sulphate decomposes at 767° C. (1,412° F.) it is the practice in some plants to keep the roasting temperature below this point. In such plants the roasting temperature for electrometallurgy is 650 to 700° C. (1,200 to 1,290° F.); however, at the plant of the Consolidated Mining and Smelting Company of Canada, Ltd., only about 2 per cent of sulphate sulphur is needed to replace the losses, and the temperature in the modified Wedge furnaces operated on the suspension roasting principles is approximately 927° C. (1,700° F.). The sulphide content, however, is reduced to a minimum, generally under 0.2 per cent sulphur.

The roasting of the ore is commonly done in Wedge multiple-hearth furnaces, but at Trail 8 of the 25 roasters were converted to a suspension roasting process, with the result that the 8 suspension roasters produced as much calcine (roasted ore) as was produced in the original 25 Wedge roasters and all roasting by the latter was discontinued. In the suspension roasting process the furnace retains the two upper hearths on which the pulverized ore is dried. The hot dried ore leaves the drying section of the furnace below the second hearth, passes through a ball mill to break up any lumps formed while drying, and then is blown by an air blast into the main furnace chamber below the two upper drying hearths. This chamber, approximately 25 ft. in diameter and 12 ft. high, is empty except for the central rotating shaft found in all Wedge roasters. In this combustion space the ore, containing enough sulphide to act as fuel, burns somewhat as powdered coal does. Ignition occurs close to the burner mouth, and the concentrate in burning maintains a temperature of approximately 927° C. (1,700° F.). Part of the hot gaseous products of combustion pass up into the drying hearth and dry the raw concentrate. The main bulk of the hot gases, heavily laden with dust and containing 9 per cent of sulphur dioxide, leaves the combustion chamber at the bottom and passes through waste heat boilers, cyclone dust collectors, and Cottrell precipitators on to the acid plant.

In the combustion chamber of the furnace, the sulphide particles are almost completely desulphurized. One advantage of the suspension roasting process is that not as much zinc ferrite is formed. Separate particles of iron and zinc ore do not come in intimate contact in the furnace and hence have little opportunity to combine. Particles containing both zinc and iron, such as are found when the ore is chiefly marmatite, do have an opportunity to form ferrite, but, owing to the sulphating action

on the dust particles and their brief period in the hot ferritization zone, the amount of zinc combined as ferrite is noticeably reduced over that combined in the usual hearth roasters.

Although there is a considerable degree of turbulence within the combustion chamber, about 60 per cent of the total feed settles on collecting hearths at the base of the furnace. The remaining 40 per cent passes out the chamber with the gaseous products of combustion, as stated above. The material settling out on the hearth contains about 0.5 per cent sulphide sulphur and 0.4 per cent sulphate sulphur. This material being rabbled across the two collecting hearths has the sulphate sulphur reduced by oxidation to 0.3 per cent; the process can be modified so that the amount of sulphate is increased if desired. The calcine is therefore collected at three different points in the system: the hearth product just mentioned, the previously mentioned dust from the cyclone collectors, and that from the Cottrell precipitators. Each of these products has a different degree of fineness and different metal and sulphur content. The net combined product, ready to be sent to the leaching plant, contains 57.3 per cent Zn; 3.7, Pb; 12.8, Fe; 2.3, S (of which 1.7 is sulphate S) with 87.5 per cent of the zinc soluble in the leaching solution.

The Leaching Process. The roasted ore, called calcine, is subjected to an acid leaching process to remove as much of the zinc as practicable. The leaching solution is a sulphuric acid solution, which is the spent electrolyte from the electrolysis tanks. That is, as in the electrometallurgy of copper, the acid goes through repeated cycles of leaching to dissolve the zinc from the calcine, followed by the electrolytic deposition of the zinc with accompanying regeneration of the acid, then back to another leaching process.

Some companies use a low acid concentration, corresponding to 100 to 130 g. per liter of acid, when the solution leaves the electrolysis cells. The low-acid process is used by the Anaconda Copper Mining Company,¹⁹ Great Falls, Montana, and by the Consolidated Mining and Smelting Company of Canada, Ltd.,²⁰ Trail, British Columbia. Other companies use higher acid concentrations of 280 g. per liter and a correspondingly higher current density in the tank house. The high-acid process was used by Evans-Wallower Zinc Company,²¹ East St. Louis, Illinois, and is used by the Sullivan Mining Company,²² Kellogg, Idaho.

¹⁹ F. Laist, F. F. Frick, J. O. Elton, and R. B. Caples, *Trans. Am. Inst. Mining Met. Engrs.*, **64**, 699 (1920).

²⁰ W. M. Archibald and associates, *loc. cit.*

²¹ U. C. Tainton and D. Bosqui, *Trans. Am. Electrochem. Soc.*, **57**, 241 (1930).

²² U. C. Tainton, *Eng. Mining J.*, **126**, 856 (1928).

A flow sheet of a low-acid process is shown in Fig. 70. The process differs at various plants but the flow sheet given has many points in

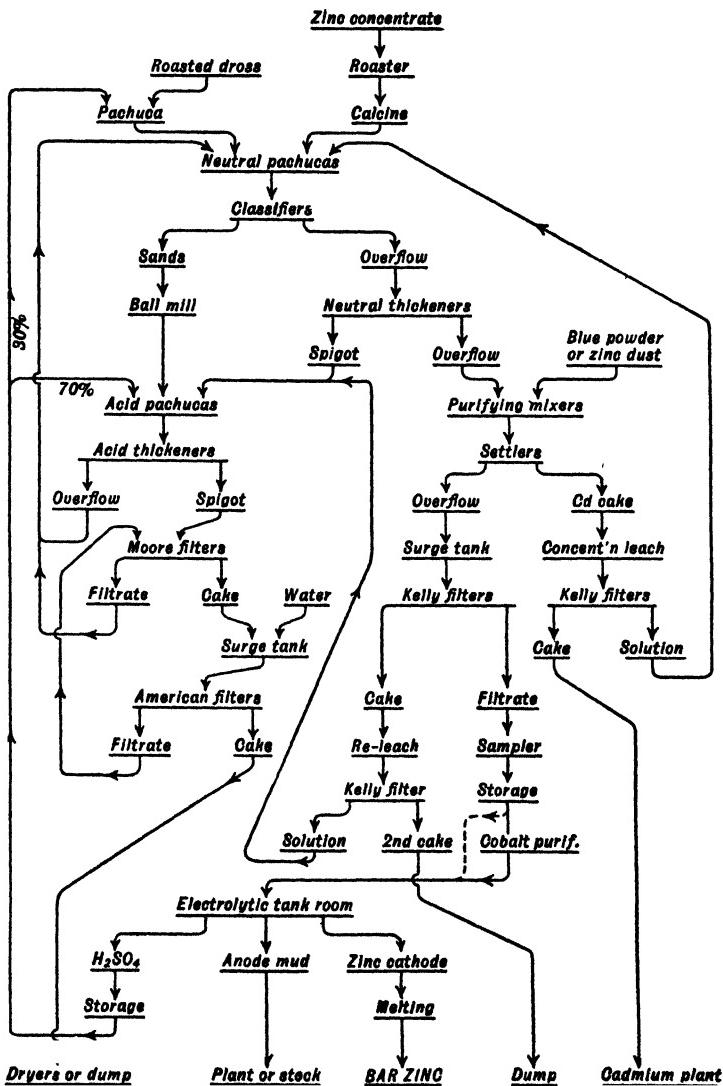


FIG. 70. Zinc plant flow sheet, low-acid process, at The Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

common with those of other plants. The leaching cycle is a double leaching process having an acid side and a neutral side.

On the neutral side, excess roasted ore is added to the slightly acid solution from the acid leach to be mentioned later. The solution becomes

neutral and with excess calcine present precipitates impurities such as iron, arsenic, antimony, and silica. The iron is precipitated as ferric hydroxide, $\text{Fe}(\text{OH})_3$. The ore and solution are brought into intimate contact in pachuca tanks, which are vertical cylindrical tanks with conical bottoms. Each tank has a central agitation column as shown in Fig. 71, through which compressed air is forced at a pressure of about 30 lb. per sq. in.

This circulates the acid-calcine mix, called pulp, and produces a thorough mixing. The neutral solution (overflow from neutral thickeners) is further treated with zinc dust to remove copper and cadmium. The zinc dust can be made by blowing air through molten zinc, but improved dust made from melting-room dross in an electric-arc furnace using coke for reduction is finding extensive application for this purpose. The average particle size of the dust is less than 5 microns, and it is much more efficient pound for pound than the air-atomized dust.²³

Cobalt is partially removed from the purified solution with nitroso beta naphthol, which is produced at the plant from sodium nitrate and beta naphthol dissolved in caustic soda. The cobalt content is maintained between 3

and 4 mg. per liter. In suitable amounts it is valuable in reducing the lead tenor of the cathode zinc and in reducing corrosion of the lead anode, but if present in excessive amounts it causes serious reduction in current efficiency. The neutral and purified zinc sulphate solution, after filtering, is ready for the electrolysis cells.

On the acid side, the partially leached solids from the neutral side are treated with regenerated sulphuric acid from the electrolysis cells to extract all the remaining soluble zinc that can be extracted, but at best the total zinc recovery is usually under 90 per cent. The resulting solution, slightly acid ($\frac{1}{2}$ to 1 per cent free acid), recycles to the neutral

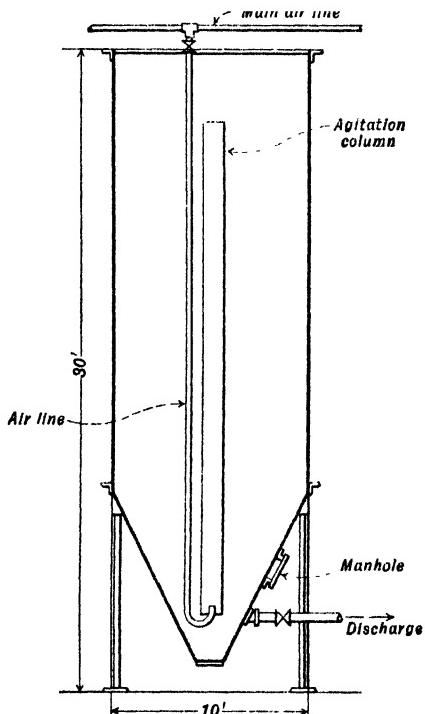


FIG. 71. Pachuca tank in section.

²³ B. A. Stimmel and associates, *loc. cit.*

side. The solids from the acid leach are filtered, washed, and rejected from the plant.

As previously mentioned, a high-acid process, called the Tainton process,²⁴ has been developed in which the acid concentration is 280 g. per liter instead of about 120 g. per liter as in the low-acid process. The advantages claimed for the high-acid process are as follows:²⁵ The acid will dissolve zinc ferrite, which does not readily dissolve in a low-acid solution; it increases the percentage of zinc and copper extraction; it dissolves more iron, which on neutralization of the solution causes greater removal of arsenic and antimony; it improves filtration, for it does not form a highly gelatinous silica precipitate; it allows the treatment of ores containing large quantities of cobalt and nickel without the addition of extra equipment; and it reduces the quantity of pulp to be agitated and filtered and the amount of solution to be purified and stored.

The roasting and grinding process is similar to that of the low-acid process, except that it is not necessary to pay as close attention to a low zinc ferrite production in the roasters. The process is shown in the flow sheet in Fig. 72.

The calcine is treated with return electrolyte in an agitator. The agitator consists of a lead-lined, flat-bottomed, round tank made of wood staves with a mechanical stirring device. A tank 20 ft. in diameter and 12 ft. deep will hold 100 fluid tons²⁶ of solution, which is sufficient for the production of 18 net tons²⁷ of metallic zinc.

The agitator is first partially filled with hot return electrolyte, which contains about 28 per cent of free acid.²⁸ It is desirable from the standpoint of coagulating silica to have the pulp (i.e., the calcine-acid mixture in the agitator) near its boiling temperature. The return electrolyte is therefore heated to about 60° C. (140° F.). This heat is obtained from the hot water coming from the roaster cooling system. The reactions in the agitator later produce enough heat to bring the temperature of the pulp near its boiling point. The ferrite is added to the acid in the agitator to the extent of about one-half of what it is estimated the charge will take. The agitator is operated for about half an hour, after which a little

²⁴ W. G. Woolf and E. R. Crutcher, *Trans. Am. Inst. Mining Met. Engrs.*, 121, 527 (1936).

²⁵ U. C. Tainton and L. T. Leyson, *Trans. Am. Inst. Mining Met. Engrs.*, 70, 503 (1924).

²⁶ One fluid ton = 32 cu. ft.

²⁷ One net ton = 2,000 lb.

²⁸ The expression per cent of acid, as used here, represents ordinary plant practice and is not a true percentage. What is meant by x per cent of acid is x grams of acid per 100 cc. of solution; thus 28 per cent acid represents 280 g. per liter H_2SO_4 . See *Trans. Am. Inst. Mining Met. Engrs.*, 70, 494 (1924).

ground manganese ore, MnO_2 , is added to oxidize the iron. The iron is oxidized to the ferric state so that, when the solution is later neutralized by the addition of more calcine, the iron will precipitate as $Fe(OH)_3$ and can then be removed by filtration.

The calcine is added until the solution is neutral, which is the point at which the iron in the solution is almost eliminated. This is determined

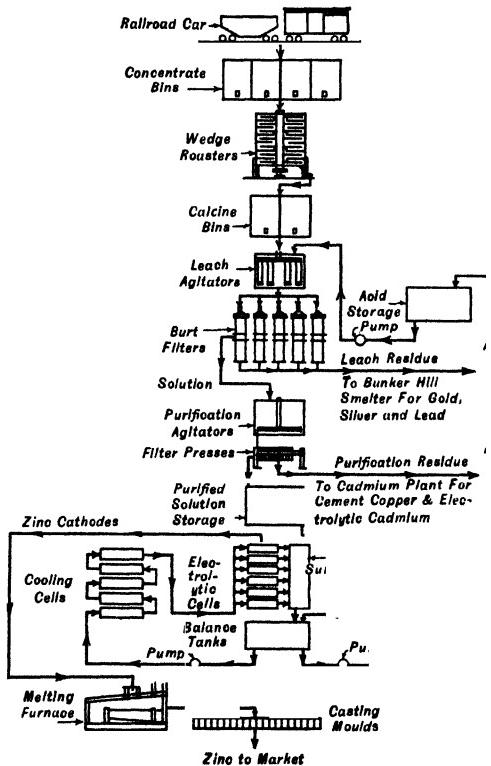


FIG. 72. Zinc plant flow sheet, high-acid process.

by allowing a drop of the pulp to fall on a thiocyanate (potassium sulphocyanate, $KCNS$) paper. As long as iron is present, a red ring is obtained. It is important not to add calcine beyond this point or the filtrate later will become milky owing to the formation of basic salts.

The pulp is then filtered and pumped to another agitator where zinc dust is added to the leach solution to precipitate copper and cadmium. The solution is again filtered and is then ready for the electrolytic plant.

Electrolytic Plant. The only commercial method known to precipitate zinc from solution is by electrolysis; the purified solution from the leaching process is therefore subjected to electrolysis at all plants. An

electrolytic zinc plant is shown in Fig. 73. Since zinc is very electronegative to hydrogen it would be expected that it would be impossible to plate zinc from an acidified zinc sulphate solution except possibly at a very low current efficiency. The hydrogen overvoltage on zinc, however, is sufficiently high that the zinc plates preferentially. However, the presence of certain metallic impurities such as copper, arsenic, antimony, germanium, tellurium, and cobalt lower the hydrogen overvoltage and cause definite loss of current efficiency with corresponding evolution of hydrogen.

The electrolysis tanks are constructed either of wood, lined with lead, or of reinforced concrete, lined with a $\frac{3}{4}$ - to $1\frac{1}{2}$ -in. layer of mixture of sulphur and sand, but linings of soft rubber are coming into use and are giving excellent service. At the plant of the Consolidated Mining and Smelting Company at Trail, B. C., some of the tanks are made in a single large casting of Prodrorite, reinforced with wire. The mixture consists of Prodrorite pitch, asphalt, quartz flour, quartz sand, and quartz pea gravel. The tanks generally are not over 10 ft. long, and are from 27 to 34 in. wide and from 36 to 55 in. deep.

The current density is 30 to 40 amp. per sq. ft. (3.2 to 4.3 amp. per sq. dm.) at plants using the low-acid solution and 100 amp. per sq. ft. (10.7 amp. per sq. dm.) at those using the high-acid solution. With the high current density the heating effect of the current is sufficient to raise the temperature of the electrolyte appreciably. The hydrogen overvoltage, and consequently the current efficiency, fall with increasing temperature. It is therefore desirable to hold the temperature between 30 and 40° C. (84 to 104° F.). This makes it necessary to cool the electrolyte. This is done either by placing cooling coils in the electrolysis tanks or by passing the electrolyte around cooling coils before it enters the tanks. The solution will deposit manganese dioxide and calcium sulphate on any cold surface, and provision must be made for removing this deposit from the cooling coils; it may be removed by brushing with a stiff broom.

The anodes are sheets $\frac{1}{8}$ in. to $\frac{1}{4}$ in. thick made of pure lead or of a lead alloy containing 99 per cent lead and 1 per cent silver. In the Tainton high-acid process two anodes are placed between each pair of cathodes; the anodes are perforated below the solution line, the perforations aiding in the circulation of the electrolyte and in reducing the spray formed.

The cathode starting sheets are made of aluminum; the side edges of the aluminum sheets fit into grooved strips in the sides of the tanks. These grooves help to hold the cathodes in place and prevent the zinc from plating around the edges, which would hinder the stripping of the

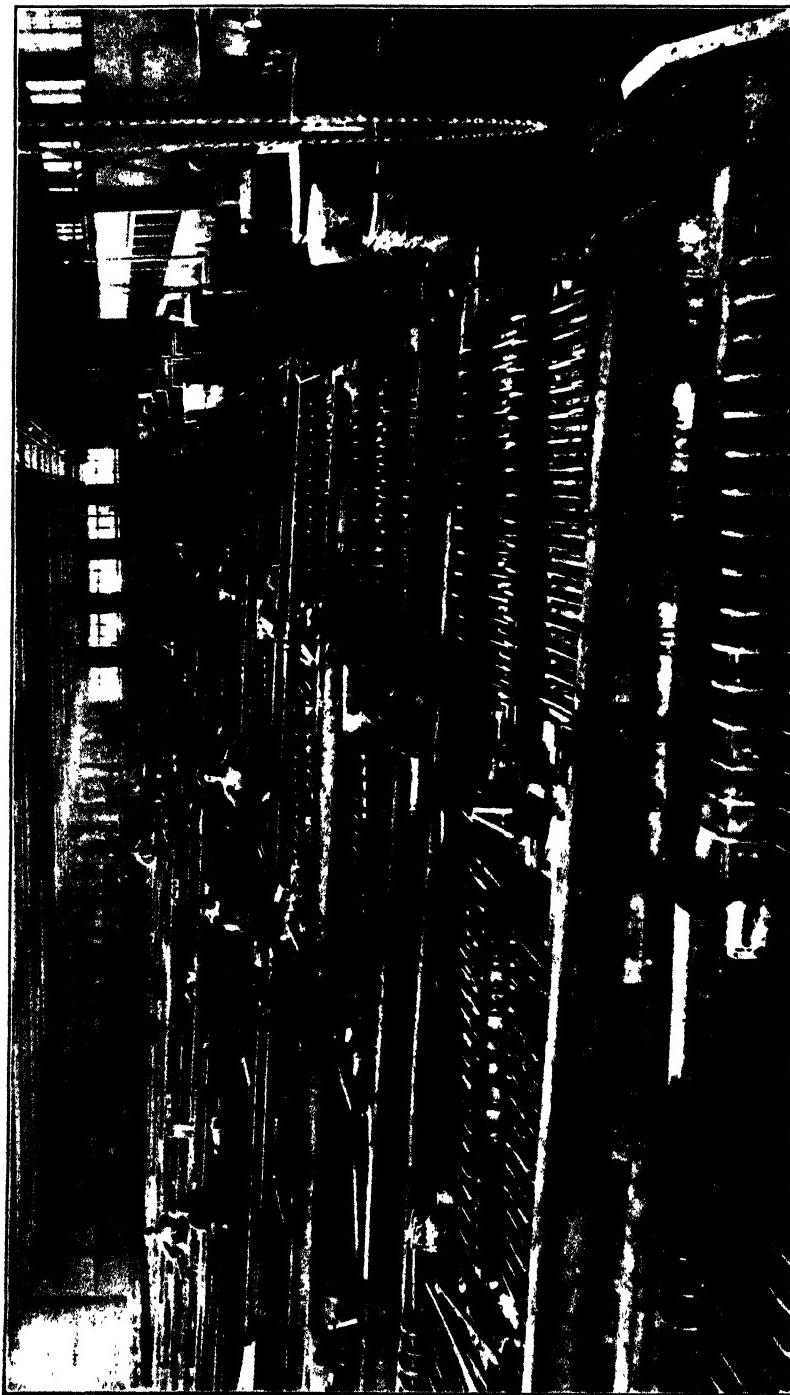


FIG. 73. Electrolytic zinc tank room. (*Courtesy the Consolidated Mining and Smelting Company of Canada, Ltd.*)

deposited zinc from the aluminum. The cathodes are removed for stripping at the end of 12, 24, or 48 hr.

The use of aluminum starting sheets was one of the important factors contributing to the successful development of the electrolytic process. In the early experiments, starting sheets of zinc were used, which followed the practice in copper and lead electrolysis. The advantages of aluminum starting sheets over zinc sheets have been summarized by Woolf²⁹ as follows. Rolled zinc starting sheets when placed in the electrolyte corrode rapidly, and the deposits are usually irregular and rough, while electrolytically formed starting sheets warp as the deposit builds on them. In electrolytic zinc cells the electrode spacing is kept at a minimum so that slight warping causes short circuits between electrodes which results in low current efficiency and corroded deposits. Furthermore, in zinc electrolysis the cathodes are removed quite frequently for stripping. Zinc starting sheets would need to be trimmed and clipped to supporting bars before being placed in the cells. Aluminum starting sheets require no such labor and are superior in this respect from the standpoint of economy.

In the high-acid process the electrolyte passing to the electrolysis cells contains 200 to 220 g. per liter of zinc; in the low-acid process the zinc concentration is about 100 g. per liter. The electrolyte is introduced into the cells continuously and electrolyzed until the zinc concentration has been sufficiently reduced. As the zinc content is reduced the acid is regenerated. The appearance of the solution, the size of the gas bubbles, and the degree of the pungent odor of the acid mist help in detecting abnormally high acid cells. If the zinc is allowed to become nearly depleted in any cell, the hydrogen will take fire and small, rapid explosions result. In the high-acid process the sulphuric acid in the solution leaving the electrolysis tanks amounts to 280 g. per liter; in the low-acid process the acid concentration is about 100 to 125 g. per liter.

During the electrolysis, manganese dioxide is precipitated, and part or all of it will settle to the bottom of the tanks. Part of it may deposit on the anodes, from which it must be removed periodically. Part of it may leave the tank as a suspension in the electrolyte, in which case it is recovered by filtration. The tank mud consisting mainly of manganese dioxide is removed periodically.

It has generally been considered that it is desirable to have the electrolyte so pure that addition agents are unnecessary. According to Tainton,³⁰ however, glue or some other colloid is absolutely essential

²⁹ Personal communication from W. G. Woolf, Kellogg, Idaho.

³⁰ U. C. Tainton and L. T. Leyson, *op. cit.*, p. 518.

to the production of smooth deposits of zinc at high current densities, no matter how pure the solution may be. In addition to forming smooth, dense deposits, glue raises the overvoltage of hydrogen on the cathode; about 3 lb. of glue is added to the electrolyte for each ton of zinc produced. In place of glue one plant uses a combination of sodium silicate and an emulsion of cresylic acid and gum arabic, which not only serves as an addition agent but also forms a tough semi-permanent froth on the surface of the electrolyte. This minimizes the evolution of acid mist so that mouth and nose masks are unnecessary.

Impurities in the Electrolyte. The effect of the impurities in the solution on the nature of the deposit, and the operating efficiency and difficulties, have been reported by Laist and his associates³¹ and by Hansen.³² The impurities may be non-cumulative, such as copper, cadmium, arsenic, antimony, iron, manganese, silica, and alumina; or cumulative, as the alkali metals, magnesium, nickel, cobalt, and vanadium.

Of the non-cumulative impurities iron, silica, and alumina are present only so far as the solutions have not been properly oxidized and the colloids coagulated. Manganese passes through all the purification processes but is precipitated on the anode as manganese dioxide, and possibly precipitates part of the cobalt in the electrolysis cells. Copper and cadmium are largely precipitated by metallic zinc in the purification process. Copper present in the electrolyte in amounts under 10 mg. per liter has no effect on the deposit. Cadmium in amounts up to 0.6 mg. per liter has no effect on the current efficiency or the character of the deposit. Cadmium contaminates the cathode in proportion to the amount present. For instance, if 50 per cent of the zinc is deposited per cycle, about 50 per cent of the cadmium is also deposited. Elements that lower the hydrogen overvoltage on zinc, such as copper, arsenic, antimony, germanium, tellurium, and cobalt, cause definite loss of current efficiency. Germanium and tellurium when present to the extent of a small fraction of one part per million cause serious evolution of hydrogen with a corresponding reduction in current efficiency.

The cumulative impurities may become quite bothersome. As the solutions are circulated through leach plant, cell room, and leach plant again these impurities steadily accumulate. Magnesium, sodium, and potassium have little effect in the electrolysis tanks in the concentrations found. Nickel, cobalt, and vanadium reduce the current efficiency, but their behavior beyond that is not fully understood.

It was once considered desirable to have a solution in the electrolysis cells that contained only zinc sulphate. Pure solutions yield excellent

³¹ F. Laist and associates, *op. cit.*, p. 729.

³² C. A. Hansen, *Trans. Am. Inst. Mining Met. Engrs.*, 60, 222 (1919).

deposits that are without blemish on the back or starting-sheet side. However, the protective action of cobalt and iron in limited amounts to act as depolarizers is recognized for preventing disintegration of the lead anodes. Antimony to the extent of 0.1 mg. per liter seems to have a beneficial effect on zinc deposition and sometimes is added to the finished electrolyte.²²

The Zinc Cathodes. The electrodeposited zinc has a high purity, generally above 99.95 per cent. The zinc cathodes after being stripped from the aluminum starting sheets, are sent to the refinery to be melted. A problem in the melting of zinc lies in the fact that, no matter what type of furnace is used, zinc oxide will form and act as an insulating layer between the metal and the source of the heat. Moreover, electrolytic zinc contains many times its own volume of hydrogen, so that, as the cathodes are pushed below the surface of the molten metal, the hydrogen is evolved and produces a froth that oxidizes very easily. An attempt is made to keep the furnace atmosphere reducing, but about 3 to 4 per cent of the zinc has to be removed as dross. Some ammonium chloride (sal ammoniac) is added in some plants to help the segregation of the globules of zinc. The dross is leached with acid electrolyte, but as the chlorine would be harmful when returned to the system the dross is first given a heat treatment in another furnace to eliminate the chlorine. The melting of the cathodes is done in reverberatory or in electric furnaces.

Electrogalvanizing Wire from Leach Solution. It is possible to electrogalvanize directly from the leach solution without the intermediate production of zinc anodes. The process as described by Tainton²⁴ and by Winkler²⁵ is applied to the galvanizing of wire. Coils of wire are butt-welded for continuous processing. A particular development is the practically simultaneous lead annealing and caustic cleaning operation performed by passing the wire through molten lead on which lies a covering bath of molten caustic. The wire is made cathodic in this caustic cell so that sodium is discharged on the wire where it removes silicon, sulphur, and phosphorus and reduces the iron oxide to the metallic state. The combined annealing and cleaning tank through which the wire passes continuously is a steel pan 20 ft. long, 24 in. wide, and 12 in. deep. From the annealing and cleaning unit the wire travels through a rinse into an acid solution where it is given an anodic treatment.

Calcined zinc concentrate containing about 69 per cent zinc is brought as raw material to the leaching plant, which is adjacent to the plating plant. The calcine is leached with spent electrolyte from the cells, which

²² W. H. Hannay and J. Bryden, *Trans. Can. Inst. Mining Met.*, 1934, p. 145.

²⁴ U. C. Tainton, *J. Am. Zinc Inst.*, 18, 42 (1937).

²⁵ L. W. Winkler, *Wire and Wire Products*, 16, 687 (1941).



FIG. 74. Wire galvanizing cell. (*Courtesy Bethlehem Steel Company.*)



FIG. 75. Part of a wire plating cell. (*Courtesy Bethlehem Steel Company.*)

contains about 25 per cent sulphuric acid. The solution after the leaching process is purified by treatment with zinc dust.

The plating cells are made of steel, lined with lead, and are about 55 ft. long. Eight wires pass through each cell continuously. A cell room is shown in Fig. 74 with the caustic cleaning cells in the background. A closer view of a part of a cell is shown in Fig. 75. The current density is approximately 1,000 amp. per sq. ft. Electrical contacts are provided every 3 ft. to distribute the current leaving the wire. Special insoluble anodes are used, made of an alloy of silver and lead.

From the plating cells the wire passes through rinsing baths and is then polished by a rapidly rotating burnishing machine, or sometimes by employing a very light draft in a die.

CADMIUM

Cadmium is found in small quantities in practically all ores, but its recovery is not practicable unless it is a by-product so that the major portion of the expense of manufacture is borne by some other metal more profitable commercially. Cadmium is one of the few metals recovered solely as a by-product.

Raw Material. Practically all the cadmium recovered comes from zinc, copper, and lead ores, but especially from zinc ores, which on the average contain about 1 part of cadmium to 200 parts of zinc. The cadmium may be obtained in more concentrated form from three sources: (1) in the bag-house condensation products from lead and copper refineries; (2) in the blue powder in zinc distillation furnaces; (3) in the "purification residue" in electrolytic zinc plants, obtained when powdered zinc is added to the leach solution to precipitate out copper, cadmium, and other impurities. When the cadmium plant of the United States Smelting, Refining and Mining Company ¹⁶ at Kennett, California, was in operation the cadmium was obtained from the bag-house condensation product from their copper furnaces. The analysis of this raw material approximated 0.55 per cent cadmium, 19 per cent zinc, 6.6 per cent arsenic, and smaller amounts of other metals. At their Midvale, Utah, plant, the cadmium accumulates in the blast-furnace flue dust. The dust in the form of briquettes is returned to the furnace time and time again for retreatment. The proportion of cadmium gradually builds up, and when it reaches about 18 per cent the dust is withdrawn for treatment in the cadmium plant.

¹⁶ H. R. Hanley, *Chem. Met. Eng.*, **23**, 1257 (1920).

The Anaconda Copper Mining Company ³⁷ at Great Falls, Montana, the Sullivan Mining Company ³⁸ at Silver King, Idaho, and the Consolidated Mining and Smelting Company of Canada, Ltd., at Trail, British Columbia, use the purification residue from their electrolysis zinc plants as the crude material for their cadmium recovery. The blue powder for recovery of cadmium is used particularly in Germany and Poland.

Leaching and Purification Processes. At the Kennett plant, which is no longer in operation, the bag-house condensate was leached with a sulphuric acid solution giving a solution containing 96 g. per liter zinc, 8 g. per liter copper, 5 g. per liter cadmium, 2 g. per liter iron, and lesser amounts of other metals. The leach solution was neutralized with powdered limerock, CaCO_3 , and agitated by air, which precipitated the iron and arsenic and about 40 per cent of the copper but none of the cadmium. The solution after neutralization contained about equal amounts of copper and cadmium. Zinc dust was then added which produced a black mud precipitate containing 25 per cent copper, 25 per cent cadmium, and 30 per cent zinc.

The precipitate was again leached with an acid solution containing 250 g. per liter of sulphuric acid, which leached zinc and cadmium from the precipitate. In order to prevent leaching of copper, care was exercised not to allow the precipitate to become dry with consequent formation of copper oxide. The leaching reduced the acid content of the solution to 10 g. per liter. The greater part of the acid was then neutralized with limerock, after which hydrated lime, $\text{Ca}(\text{OH})_2$, was added to neutralize the remaining acid. The copper residue was removed by filtration and returned to the copper plant.

The cadmium was precipitated from the solution by sheet zinc. The solution became depleted of cadmium but richer in zinc, and was sent to the electrolytic zinc plant for recovery of the zinc. The cadmium sponge was washed and dissolved in return electrolyte from the cadmium electrolytic tanks. When the cadmium content of the solution amounted to 90 to 100 g. per liter it was treated for removal of iron. This was accomplished by the addition of hydrated lime, air agitation being used to oxidize the iron. The iron, as the hydrate, was removed by filtration and the solution was delivered to the feed tank which supplied the electrolysis cells.

At the Great Falls and Silver King plants, the feed to the cadmium plant is the purification residue. This, as explained under the metallurgy of zinc, is obtained when the zinc leach solution is purified by the addi-

³⁷ W. E. Mitchell, *Trans. Am. Inst. Mining Engrs.*, 1930, p. 239.

³⁸ W. G. Woolf and R. M. Miller, *Mining Congr. J.*, 17, 626 (1931).

tion of powdered metallic zinc. This action removes the cadmium together with other impurities, chiefly copper, nickel, and cobalt, as finely divided metallic material known as purification residue. This residue also contains about 40 per cent excess zinc.

This residue is treated to recover the cadmium, copper, and zinc. The mass is therefore leached with a sulphuric acid solution which is the spent electrolyte from the zinc electrolysis cells. In order to make the above metals more soluble in the acid and to render the iron, arsenic, and antimony insoluble, at Great Falls the precipitate is roasted prior to leaching, but at Silver King it is merely ground in a ball mill before leaching. At the first-named plant the leaching solution contains 10 to 12 per cent free sulphuric acid; at the other plant, 27 per cent acid. The leaching is done in large lead-lined tanks with mechanical agitation. The zinc and cadmium are dissolved and the copper remains as cement copper, which is removed and sent to the copper smelter.

If the filtrate, after the undissolved copper has been removed, still contains appreciable amounts of copper, zinc dust is added carefully to precipitate all of it. The solution after filtration still contains cadmium and zinc.

At Great Falls the cadmium is precipitated by the addition of zinc dust. The precipitate called cadmium sponge is removed by filtration. At Silver King the solution is passed over zinc plates where the cadmium precipitates as a metal sponge. The sponge floats to the surface, is scraped into launders, and filtered and washed in Burt filters. The solution containing mainly zinc is returned to the zinc plant.

The cadmium sponge is contaminated with zinc, nickel, cobalt, lead, and iron, and must be redissolved and electrolyzed to produce commercial cadmium.

The sponge after washing is stored in piles for two or three weeks to allow partial but not complete oxidation. Unoxidized cadmium sponge dissolves very slowly in dilute sulphuric acid, but the oxidized material dissolves quite readily. The oxidized sponge is dissolved in return electrolyte from the cadmium electrolysis cells. The sponge before solution is not completely oxidized in order that it may contain sufficient metallic cadmium to precipitate any copper that may have gotten past the leach.

After being dissolved, the cadmium in the form of a neutral solution is sent to a storage tank and is ready for electrolysis.

At the Midvale plant of the United States Smelting, Refining and Mining Company, the flue dust from the zinc blast furnaces is roasted at a low heat to volatilize the arsenic. The sinter containing about 20 per cent cadmium is crushed in a ball mill and then treated with sul-

phuric acid. The pasty mix is charged into reverberatory furnaces for 24 hr., using pulverized coal. A soluble sulphate is formed which is ground in a ball mill and charged into a pachuca tank containing spent electrolyte and water. The solution is neutralized with hydrated lime, filtered, and sent to the electrolytic room.

Electrolytic Room. In the electrodeposition of cadmium difficulty is experienced in obtaining dense, smooth deposits. If a neutral solution is used the deposit will be of a spongy mass which melts with difficulty. In acid solutions a coherent deposit is obtained but with the formation of "trees," sponge, and sprouts.

At the Kennett plant fairly smooth and firm deposits were obtained by means of rotating cathodes. The tanks were semicylindrical in shape, placed horizontally. The lead anodes were in the shape of segments of circles somewhat less than half a circle, and were supported by double grooved porcelain blocks resting on the lead lining of the cell. The anodes were entirely submerged except for a portion which connected with copper bars which in turn connected with the anode bus. There were two anodes for each cathode.

Cathodes consisted of aluminum discs 4 ft. in diameter and $\frac{3}{16}$ in. thick. These were mounted on aluminum hubs which were slipped onto a 4-in. steel shaft; the aluminum hubs completely covered the shaft and thus protected it from corrosion.

The anodes were 4 in. apart, the anodes and cathodes being spaced $2\frac{1}{2}$ in. center to center. This gave a clearance of 9 in. between cathode discs, which was ample to permit easy stripping of the deposits without removing the discs from the shaft. There were nine cathode discs to a cell.

For conducting the current from the rotating shaft to the cathode bus a copper-faced steel pulley was mounted on one end of the shaft with radial copper strips connecting the face to the shaft. High-conductivity brushes placed in contact with the pulley face conducted the current to the cathode bus.

With a current of 1,200 amp. per cell, the current density was approximately 15 amp. per sq. ft. (1.6 amp. per sq. dm.). A higher current density produced a rough deposit. The average e.m.f. was 4 volts per cell. The cathodes rotated at about $1\frac{1}{2}$ r.p.m.

The cells were operated in batches. When the spent electrolyte had been drained, fresh leach solution was introduced. The solution was slightly acidified with acid electrolyte to avoid the initial spongy deposit which would be formed if electrolysis were started with a neutral solution.

At the Great Falls and Silver King plants stationary cathodes are used with satisfactory results. The cells, anodes, and cathodes are of a type similar to those used for zinc electrolysis.

At the Great Falls plant of the Anaconda Copper Mining Company each cell contains 27 lead anodes and 26 aluminum cathodes. In view of the fact that cadmium deposits tend to form trees, a low current density of 4 amp. per sq. ft. (0.43 amp. per sq. dm.) at 2.6 volts is used. The optimum temperature for electrolysis is 30° C. (86° F.). Each cell has an individual solution feed, and the spent electrolyte discharges into a common collecting launder. The cells are lead lined. A cadmium cell is shown in section in Fig. 76.

The feed contains 100 to 120 g. per liter of cadmium and 80 g. per liter of zinc; the spent electrolyte about 70 to 80 g. per liter of sul-

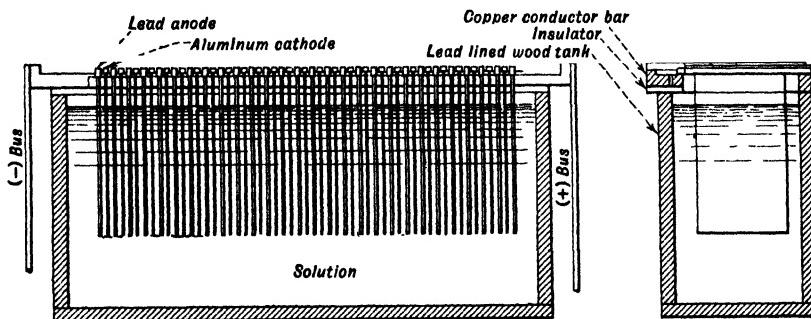


FIG. 76. Section of cadmium electrolysis tank cell.

phuric acid. Glue is added to the electrolyte to reduce the formation of beads; about 10 lb. of glue is used per ton of cathodes. The electrolyte is kept at a temperature of about 35° C. (95° F.). The ampere efficiency ranges between 80 and 90 per cent.

The cathodes are stripped every 24 hr., one plate being lifted out at a time. The spent electrolyte is returned to the tanks for leaching cadmium sponge. In order to keep the zinc content from building up too high, a certain amount of electrolyte is replaced with fresh acid. It may be concentrated sulphuric acid, or if this is not available spent zinc electrolyte is depleted to a low zinc content.

Rotating cathodes reduce the formation of trees but are not used to any large extent. Most of the cadmium electrolysis cells are similar in construction to the zinc deposition cells, and treeing is kept down, but not eliminated, by the use of a low current density and by glue in the electrolyte. The Electrolytic Zinc Company of Australasia, Ltd., uses cells with rotating cathodes for cadmium deposition.

Disposition of the Cathodes. The cathodes and trees are melted under a thin layer of sodium hydroxide to prevent excessive oxidation. The melting is done in cast-iron pots of about 1,000-lb. capacity, in one plant heated electrically to a temperature of 400 to 500° C. (752 to

932° F.). The caustic soda becomes viscous from oxidized cadmium and is replaced occasionally. About 40 lb. caustic is used per ton of metal cast.

The caustic slag, containing cadmium oxide and a large amount of cadmium beads and shot, is leached with water to dissolve the excess sodium hydroxide. The oxide and beads are then dissolved in sulphuric acid, and the leach solution, after filtration, is fed to the electrolysis cells.

The cadmium is tapped from the pots and cast into bars weighing approximately 75 lb. These bars are remelted and the cadmium cast into marketable shapes, such as pencils, slabs, and anode sheets, but a large part of it goes into balls 2 in. in diameter, for use in the plating industry, as shown in Fig. 51, p. 123.

MANGANESE

Manganese is produced electrolytically by the Electro Manganese Corporation, Knoxville, Tennessee, by a process in which the ore is leached to produce a manganous sulphate solution. This solution after purification is electrolyzed, giving a deposit of manganese metal with a purity of 99.94 per cent and better. The process has been described by Hammerquist.³⁹

High- or low-grade ores can be used as the raw material, and it is anticipated that much of the domestic manganese ore once considered useless will become a reliable source of manganese. With the exception of the carbonates (rhodochrosite) the native ore is not soluble in sulphuric acid. In the majority of the ores the manganese occurs as the dioxide or some other form in a higher state of oxidation, and these ores must be given a reducing roast before leaching.

The ground ore is fed continuously into an electric furnace against a countercurrent flow of producer gas. The reduced ore is stored in air-tight cans to prevent reoxidation.

Since manganese is relatively high in the electromotive series, impurities more electropositive must be removed before electrolysis to prevent their deposition with the manganese.

The reduced ore is leached with spent electrolyte which contains 150 g. per liter of ammonium sulphate and approximately 25 g. per liter of sulphuric acid and a small amount of manganous sulphate; the solution is fortified with the proper amount of sulphuric acid and, if necessary, with

³⁹ W. L. Hammerquist, *Steel*, 105, 42 (1939). Other references: J. Koster and S. M. Shelton, *Eng. Mining J.*, 137, 510 (1936); S. M. Shelton and M. B. Royer, *Trans. Electrochem. Soc.*, 74, 447 (1938); U. S. Bur. Mines Repts. Investigation 3322 (1936), 3406 (1938), 3477 (1939), and 3580 (1941).

ammonium sulphate, so that the final solution after leaching contains 150 g. per liter of ammonium sulphate and 70 g. per liter of manganous sulphate. The crude leach solution is then filtered and made basic by the addition of gaseous ammonia. Air is blown into the solution to accelerate the oxidation of iron. Most of the iron is precipitated as ferric hydroxide; arsenic is combined chemically or adsorbed in the precipitate of iron hydroxide. If the original iron content is less than 0.1 g. per liter, metallic iron or ferrous sulphate must be added. The solution is allowed to stand 3 to 4 hr. and is then filtered.



FIG. 77. Cells for the electrolytic production of manganese.

The filtrate is treated with ammonium sulphide in a lead-lined tank where there is an immediate precipitation of a mixture of cobalt, nickel, iron, and manganese sulphide, and the sulphides of any other heavy metals that may be present. The solution is allowed to stand 6 to 12 hr. for the purification reactions to go to completion, and when upon test it is found to be free from impurities it is filtered and pumped to the catholyte storage tanks.

The solution now contains only manganous and ammonium sulphates and traces of ammonium sulphide and a few soluble metal sulphides. The alkaline solution, however, is unstable, and, to prevent the oxidation of manganese with consequent precipitation of manganese dioxide, sulphur dioxide is added until its concentration in the solution reaches 0.1 g. per liter. High purity as regards metals more electropositive than manganese is essential. Their presence in amounts that can be detected only spectroscopically may still cause serious trouble in the cell room.

The purified solution is electrolyzed in laminated wood cells, lined with a phenol plastic. Each cell is 96 by 28 by 43 in. and has a capacity of 27 lead anodes and 26 cathode compartments. The cathode compartments are constructed of oak covered with a canvas diaphragm. Each compartment is slotted to accommodate a stainless-steel cathode, 36 by 18 in. The purified solution is fed into the cathode compartment.

The current density is 35 to 40 amp. per sq. ft. at 5 volts. The metallic manganese is deposited on the stainless-steel cathode, from which it is stripped after washing and drying. The cathodes are left in the cell from 32 to 40 hr. and have from 12 to 15 lb. of manganese deposited on them when withdrawn. Figure 77 shows an installation of manganese cells with a cathode partly withdrawn for inspection. Twenty-four cells are connected in series, and the cell block will produce 4,000 lb. of pure manganese per day.

IRON

The electrometallurgy of iron has not found commercial application up to the present time. However, the successful electrodeposition of iron suggested the idea that electrolytic iron might be made directly from the ores. Accordingly, an experimental plant was constructed at Milford, Connecticut.⁴⁰

The ore used was hematite, Fe_2O_3 , limonite, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, or pyrrhotite of the approximate formula Fe_7S_8 , and was ground to pass 200 mesh. The leaching cycle was countercurrent and was divided into two steps. The fresh ore was leached with a weak anolyte containing 10 g. Fe^{+++} ions per liter. The iron in the leach solution was then reduced with sulphur dioxide. The pulp, consisting of the partially leached ore plus the solution with its ferrous iron, was passed to a Dorr thickener. The overflow was treated with scrap iron to cement out the copper. The partially leached ore was then treated with strong anolyte coming directly from the cells. This solution contained 72 g. Fe^{+++} ions per liter, the ore at the same time becoming depleted of iron. The pulp was settled in a Dorr thickener, and the overflow, now a weak anolyte, was used to partially leach more fresh ore. The solutions for both leaches was kept at 95° C. (194° F.). The primary leach required 2 hr.; the secondary leach, 6 hr.

For the leaching tanks and the electrolytic cells, wood was found entirely unsuitable, and bitumastic coverings were unsatisfactory, but concrete tanks lined with sulphur or a sulphur-coke mixture gave

⁴⁰ F. A. Eustis, *Chem. & Met. Eng.*, 27, 684-5 (1922); and D. Belcher, *Trans. Am. Electrochem. Soc.*, 45, 461 (1924).

good results. Iron pipe cannot be used for ferric chloride solutions and is not desirable for ferrous chloride solutions. Rubber and ceramic ware seem to be most suitable.

In the leaching process calcium and magnesium carbonates and zinc sulphide leach more readily than the iron sulphide. Calcium and magnesium are harmless in the electrolyte except that they represent a continual loss of effective chloride. Any zinc in the electrolyte, however, will cause some zinc to deposit with the iron, and no practicable method was found to keep the zinc content in the cathode below 0.02 per cent. The carbonates can be eliminated from the ore by a preliminary wash with a cold and very dilute sulphuric acid solution. Calcium sulphide, CaS_2 , will precipitate lead, nickel, cobalt, arsenic, and antimony.

It was attempted to make a thin tube of electrolytic iron which could be stripped from its mandrel and cut into a spiral coil for cold-rolling. Difficulties were encountered with the driving mechanism and the electrical contacts to the rotating cathode so that a cell was designed with simpler plate-type cathodes and flat graphite anodes. Both types of cell required diaphragms, for which asbestos cloth seemed most suitable. The diaphragms were a source of annoyance and expense, especially considering that in an experimental plant constant changes had to be made. Another cell was constructed somewhat like a filter press, the asbestos diaphragm filling the role of the filter cloth. This cell proved more satisfactory but still presented difficulties.

Electrolyte temperatures above 70° C. (158° F.) are desirable. Good deposits were obtained with an iron concentration in the electrolyte from 75 to 275 g. per liter. Most of the iron was deposited at 100 amp. per sq. ft. (11 amp. per sq. dm.) for rotating cathodes, and 25 amp. per sq. ft. for plate cathodes. Current efficiencies of 85 to 90 per cent were attained regularly.

Although the electrometallurgy of iron has not reached commercial application, the process looks hopeful and has been further tested on a considerable scale at Trail, British Columbia, and at the Department of Mines, Ottawa.

CHAPTER IX

ELECTROMETALLURGY THE ELECTROLYSIS OF FUSED ELECTROLYTES

The potentials and other characteristics of the ions of some metals make it difficult or impossible to obtain these metals by reduction with carbon or by electrodeposition from aqueous solution. Secondary reaction with the solvent or the preferential discharge of hydrogen is often the disturbing factor with aqueous solutions. The metallurgy of such metals has been made possible by the electrolysis of their fused compounds. The more common metals thus obtained commercially are aluminum, beryllium, calcium, cerium, Misch metal, lithium, magnesium, and sodium; the electrometallurgy of these will be discussed in this chapter. Other metals that have been obtained by this process are potassium, strontium, barium, cesium, rubidium, tantalum, radium, thallium, titanium, uranium, and vanadium. A number of these metals have been discovered by the electrolysis of their fused compounds. The compounds more conveniently employed for electrolysis are the halides, oxides, or hydrates.

In most practical applications of the electrolysis of fused compounds the melting point of the metal deposited is below the operating temperature of the bath, so that the metal is deposited in the liquid state. Aten¹ and his associates have also studied the electrolysis in the fused state in which the metal was deposited in the solid form. Their investigations were directed to the electrolysis of silver and copper salts; the melting points of these metals are appreciably higher than the melting points of their halide salts.

The conductance of fused electrolytes is ionic, and the electrode products are usually the same as when the compounds are electrolyzed in aqueous solution if, where necessary, due allowance is made for the fact that generally no water is available for secondary reactions. For example, magnesium chloride gives magnesium and chlorine; sodium nitrate gives sodium and a mixture of oxygen and nitrous gases. Sodium

¹ A. H. W. Aten, H. J. den Hertog, and L. Westenberg, *Trans. Am. Electrochem. Soc.*, 47, 265 (1925).

hydroxide gives sodium at the cathode and the hydroxyl group, OH, at the anode. Two of the hydroxyls react together to form water and oxygen. Some of the liberated sodium dissolves in the hydroxide and eventually reaches the anode where, coming in contact with the water, it reacts to form sodium hydroxide and hydrogen. This is one of the rare instances where hydrogen and oxygen are obtained at the same electrode.

The conductances of fused electrolytes are usually considerably greater than the corresponding compounds in aqueous solution at room temperature. The conductances of fused electrolytes increase with rise of temperature, almost linearly at moderate temperatures, but lag behind at higher temperatures. The effect of temperature can be accounted for essentially by its effect on the viscosity of the melt.

Conductance. The effect of temperature on the conduction of potassium dichromate and sodium nitrate,² and silver bromide and calcium chloride,³ is shown in Fig. 78. The conductivities of fused electrolytes can be determined in much the same manner as those for aqueous solutions. Owing to the action of the fused compounds on the structure of platinum black it is necessary to use unplatinized platinum electrodes.

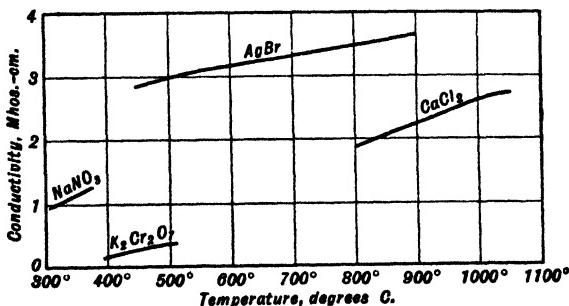


FIG. 78. Effect of temperature on the conductances of fused electrolytes.

With good conducting salts the electrodes must be separated with a capillary tube to reduce the conduction to a convenient amount.

Very little is known regarding the degree of dissociation of fused compounds. It was once supposed that dissociation was complete, but later investigations do not support this conclusion. Lorenz⁴ has calculated that the degree of dissociation of sodium nitrate is approximately 0.32 at 388° C. (730° F.). However, fused compounds of a salt-like nature, such as the halides, are assumed to be completely dissociated.

² R. Lorenz and H. T. Kalmus, *Z. physik. Chem.*, **59**, 17 (1907).

³ K. Arndt and A. Gessler, *Z. Elektrochem.*, **14**, 662 (1908).

⁴ R. Lorenz, *Z. physik. Chem.*, **79**, 63 (1912).

Decomposition Voltage. The decomposition voltage of fused compounds decreases with increase in temperature. The change in decomposition potential with temperature is shown for two salts in Fig. 79.⁵ It would be desirable, therefore, from the point of view of voltage, to use high temperatures in technical electrolysis of fused compounds, but the extra wear on the equipment and the heat lost by radiation may more than compensate for any gains made. In addition, high temperatures decrease current efficiency; the nearer the temperature to the freezing point of the electrolyte, the higher the yield of electrodeposited metal.

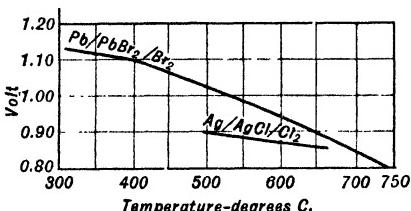


FIG. 79. The effect of temperature on the decomposition potentials of fused lead bromide and silver chloride.

In aqueous solutions so in fused electrolytes it is possible to have a fractional deposition of metals from the mixture of the salts of several metals. It is possible under suitable conditions to separate lead almost completely from zinc, silver from lead and zinc, zinc from copper, and iron from zinc.⁷

Factors Affecting Current Efficiency and Energy Efficiency. A number of factors in the electrolysis of fused compounds tend to produce a low efficiency or even prevent entirely the production of the metal. The following factors have a direct bearing on the efficiency of the operation:

Diffusion. Some metals, when liberated at the cathode, have a tendency to dissolve in the electrolyte and diffuse to the anode where secondary chemical reactions affect the yield. This is illustrated by the example already mentioned in which sodium, in the electrolysis of fused sodium hydroxide, diffuses to the anode and there combines with the water formed as the result of the liberation of the hydroxyl. At the anode, with fused lead chloride, Faraday observed the formation of lead tetrachloride.

Auerbach⁸ found that, in the electrolysis of fused lead chloride, the yields of chlorine and lead were never equal; the main source of differ-

⁵ Based on results by V. Czepinski, *Z. anorg. Chem.*, **19**, 208 (1899).

⁶ V. Czepinski, *op. cit.*, p. 208.

⁷ R. Lorenz, *Z. anorg. Chem.*, **10**, 78 (1895); *Z. Elektrochem.*, **2**, 318 (1895-6).

⁸ G. Auerbach, *Z. anorg. Chem.*, **28**, 1 (1901).

In an electrolysis cell containing fused electrolytes the reversible e.m.f. is equal to the decomposition voltage. This value depends upon the nature of the electrodes, the electrolyte, and the temperature. With mixtures of two salts the e.m.f. depends upon the concentration of salt corresponding to the metals used as electrodes.⁶ Just as

in aqueous solutions so in fused

ence was the absorption of gaseous chlorine by the electrolyte. After continued operation the electrolyte became saturated and the chlorine yield rose to nearly that of the lead.

Metal Clouds or Fogs. In the electrolysis of fused compounds there is formed at the cathode a cloud or fog which consists of fine globules of the cathode metal or of secondary products dispersed in the molten electrolyte. This fog decreases the current yield very materially. The fog appears to be colloidal in its nature⁹ and is consequently more readily attacked than the metal in its massive form. Fog usually is present in amounts under 0.1 per cent.¹⁰

The higher the temperature of the melt, the finer are the particles of the fog, and if the temperature is raised sufficiently a true solution appears to form and the melt becomes clear. On the other hand, the addition of a small amount of reducing agent can produce the effect.

The addition of certain neutral salts reduces or suppresses the tendency of fog formation. The formation of fog is one of the chief causes of loss in the deposition of a metal, so that the two effects are closely associated. Figure 80 shows how the addition of sodium chloride, potassium chloride, or barium chloride to molten lead chloride increases the current efficiency.¹¹ However, not all additions to the electrolyte increase the current efficiency, as was shown by Appelberg,¹² who found that small amounts of ferric chloride added to lead chloride reduced the current efficiency very markedly, 3.2 per cent ferric chloride reducing the efficiency of lead chloride electrolysis from 96.3 per cent to 19.8 per cent.

Anode Effect. In the electrolysis of fused salts it frequently happens that the voltage rises suddenly and the amperage decreases, and a hissing sound is heard at the anode. The anode appears to glow owing to the formation of innumerable little spark discharges. This phenomenon is known as the anode effect, the nature of which was established by v.

⁹ R. Lorenz and W. Eitel, *ibid.*, **91**, 46 (1915); and W. D. Bancroft, *Applied Colloid Chemistry*, p. 388, McGraw-Hill Book Company, New York, 1932.

¹⁰ R. Lorenz, G. v. Hevesy, and E. Wolff, *Z. physik. Chem.*, **76**, 732 (1911).

¹¹ R. Lorenz, *Z. Elektrochem.*, **13**, 582 (1907).

¹² A. Appelberg, *Z. anorg. Chem.*, **36**, 36 (1903).

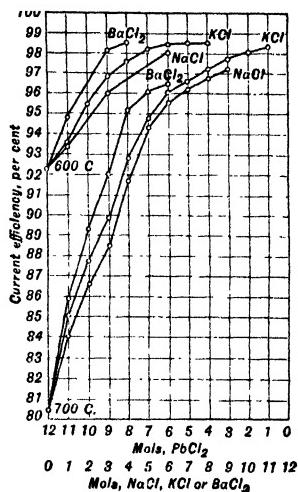


FIG. 80. Effect of certain chlorides on the electrolysis of lead chloride.

Wartenberg.¹³ The molten electrolyte seems to move away from the anode and not to wet it. The phenomenon has been described by Taylor¹⁴ as follows:

There often occurs during the electrolysis of fused salts an annoying and troublesome phenomenon known as the anode effect. During the course of the electrolysis, suddenly and without any obvious external cause, the voltage increases markedly, the amperage decreases, a soft rustling, hissing sound is heard, like the discharge of a small induction coil, the anode appears to be covered by myriads of little luminous spark discharges, and the molten electrolyte, which up to this time had been in intimate contact with the anode, shrinks away from it and does not appear to wet it. The smooth, even, normal evolution of gas from around the anode has ceased. These occurrences are summed up in the all-inclusive term, anode effect. . . . If the anode effect occurs with a fairly high frequency, rheostats and bus-bars in the circuit may chatter, rattle and vibrate, or, if the frequency is high enough, they may even give off a musical tone.

During the normal course of electrolysis gas bubbles are constantly escaping at the anode in a smooth and regular order. When the anode effect occurs the gases around the anode form a film which holds the molten electrolyte away from the anode. The current is carried from the anode to the electrolyte mainly by a large number of shifting arcs. The arcing produces local heating which causes the gases to expand with the result that the electrolyte is pushed farther from the anode. The anode effect, once started, therefore, tends to perpetuate itself.

The anode effect may be caused by any condition which will produce local overheating at the surface of the anode, particularly by a film of solid material having a high resistance which may form on the anode surface. This film may consist of frozen electrolyte formed on the anode because of local cooling—an insoluble material from the bath which has migrated to the anode and adhered to it; or it may consist of impurities left on the surface of the anode by the continued consumption of carbonaceous material. The anode effect is sometimes accompanied by loss in weight of the anode due to the formation of halides of carbon.

The anode effect is particularly noticed in connection with high current densities. It may be made to disappear by removal of the gas layer, which may be done by stirring, raising the anode from the melt for a moment, or reversing the current.

ALUMINUM

In the combined form aluminum is the most widely distributed metal. Its compounds, as found in nature, are very stable, and the separation

¹³ H. v. Wartenberg, *Z. Elektrochem.*, **32**, 330 (1926).

¹⁴ C. S. Taylor, *Trans. Am. Electrochem. Soc.*, **47**, 301 (1925).

of the metal involved difficulties that were not readily overcome. At the present time, however, aluminum plays an important part in the economic life of the world.

The present-day production of aluminum resolves itself into two major phases: the production of pure alumina, Al_2O_3 , from a suitable mineral, such as bauxite; and the reduction of the alumina to the metal by electrolysis in a bath of fused cryolite.

Nature of the Ore. Aluminum is found in practically all minerals. In sandstone and limestone it is found only as an impurity, but in most other minerals it is an important constituent. It is most widely distributed in the form of silicates such as the feldspars, micas, and clays. It occurs also abundantly in the form of the hydrated oxide, which is the most important source for industrial production of aluminum.

Bauxite is such a hydrated aluminum oxide. It is said to consist of a mixture of the alpha-monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and the trihydrate, gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, together with a number of impurities. It is believed by some that bauxite is a mineral of the composition $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, but the existence of such a compound does not seem to have been definitely established.

The commercial bauxites contain 48 to 60 per cent Al_2O_3 , 1 to 25 per cent Fe_2O_3 , 1 to 12 per cent SiO_2 , 2.5 to 3 per cent TiO_2 , and 10 to 30 per cent combined water with lesser amounts of other impurities.

In the United States the main sources of bauxite are Georgia, Alabama, Tennessee, but chiefly Arkansas. American bauxites are characterized by their low iron content.

Purification of the Bauxite. If the impure bauxite is dissolved in molten cryolite and subjected to electrolysis, most of the impurities associated with the alumina will also be reduced to metal or metaloids; these will alloy with the aluminum and thus produce an impure metal. It is therefore necessary to purify the ore so that practically all impurities are removed. The purified alumina contains above 99.5 per cent alumina. The production of pure alumina is an expensive process and is a very important item in the cost of aluminum.

A large number of processes have been developed for the production of pure alumina, but only three of the more important ones can be discussed here. In practically all, the ore is treated with an alkali which converts the alumina into sodium aluminate, $\text{Na}_2\text{Al}_2\text{O}_4$, which is soluble in water. This is filtered from the residue and treated to precipitate pure aluminum hydrate. The hydrate is separated from the solution, washed, and heated to a temperature sufficiently high to drive off all the water, producing a pure dry alumina.

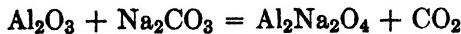
Bayer Process. The Bayer process¹⁶ is the most widely used method for producing pure alumina from bauxite and is the only one employed in the United States. The bauxite is dried to permit grinding to a powder of 80 mesh or finer. The powdered alumina is digested with a caustic solution of a concentration somewhat greater than one mole Na₂O for each mole Al₂O₃ in the ore. Increasing the temperature or the concentration of the caustic solution increases the amount of alumina dissolved; but, the more concentrated the alkali solution, the greater will be the amount of alumina retained in solution after the precipitation, and the greater will be the filtration problems in addition to the severe wear on the filter cloths.

The digestion requires a period of 1½ to 8 hr. in an autoclave at a temperature of 160 to 170° C. (320 to 338° F.). The digestion process dissolves most of the alumina but none of the iron. Silica in the bauxite, however, causes loss of both soda and alumina owing to the formation of an insoluble sodium aluminum silicate. It is therefore desirable that ores for use in the Bayer process have a relatively low silica content.

When digestion is complete, the hot sodium aluminate is filtered from the residual "red mud" in filter presses. The aluminate solution is pumped into precipitation tanks where it is agitated and slowly cooled. The solution is then diluted, and 70 to 80 per cent of the aluminum hydroxide is precipitated by hydrolysis. Some aluminum hydrate is added to initiate precipitation of Al₂O₃·3H₂O. It is desired to obtain a coarsely crystalline product instead of fines, which cause loss in subsequent drying and handling. The precipitated alumina is filtered, and washed and calcined in rotary kilns at about 1,100° C. (2,012° F.) in order to convert it to the non-hygroscopic anhydrous alumina suitable for use in the electrolytic cells.

The filtrate contains alumina and caustic soda; it is concentrated by evaporation, after which more caustic is added to bring it up to the proper strength, and is then used for digestion of a new charge.

Furnace Process. In the furnace process the finely ground bauxite is mixed with soda ash, Na₂CO₃, and the mixture is heated in a rotary kiln to a temperature of about 1,100° C. (2,012° F.). The fused sodium carbonate reacts with the alumina in the ore to form sodium aluminate:



At the same time there are also formed sodium ferrite, sodium titanate, and sodium silicate.

¹⁶ K. J. Bayer, Process for making alumina, U. S. Patent 515,895, March 6, 1894; J. A. Lee, *Chem. & Met. Eng.*, 47, 674 (1940).

The charge is then digested with a weak caustic solution at a temperature of about 80° C. (176° F.). The mixture is agitated until the maximum amount of alumina is dissolved. The sodium ferrite reacts with water to form sodium hydroxide and insoluble ferric hydroxide, Fe(OH)_3 , while the silica is mostly precipitated as sodium aluminum silicate.

The aluminate solution is filtered from the red mud precipitate, and the clear filtrate is treated for recovery of the alumina. This may be done by saturating the solution with carbon dioxide at a temperature of about 80° C. (176° F.). Instead, part of the alumina may be precipitated from the solution by the addition of a seed charge of aluminum hydrate with subsequent cooling and dilution as in the Bayer process. The precipitation is completed, in the portion of solution not needed for leaching in the next cycle, by saturating the solution with carbon dioxide. The alumina is removed by filtration, and then calcined to produce the anhydrous alumina.

In either of the above methods the alumina content of the calcined material is 99.5 per cent or above.

*Pedersen Process.*¹⁶ A mixture of bauxite, iron ore, lime, and coke is smelted in an electric furnace to produce a molten calcium aluminate slag containing about 40 per cent of alumina and only 5 to 10 per cent of silica. The slag is crushed and then leached with a hot solution containing approximately 5 per cent sodium carbonate and 0.5 per cent sodium hydroxide, forming insoluble calcium carbonate and soluble sodium aluminate. The calcium carbonate is removed by filtration, and the sodium aluminate is precipitated from the solution by carbon dioxide. The aluminum hydrate is filtered from the remaining solution and then calcined to alumina.

The Pedersen process was first used on a commercial scale at Høyanger, Norway, in 1928.

Other Processes for Producing Alumina. A number of other processes have been developed for producing pure alumina. Some of these have merit and are used abroad, but most of them have no practical application at present. The processes may be divided into the alkaline and the acid processes; those described above are alkaline. In the alkaline processes the iron is easily and completely removed, but silica elimination may become quite difficult, so that ores of low silica content must be used. In the acid process silica is not dissolved but the removal of iron from solution may present difficult problems, so that for acid processes ores low in iron are desirable. Hydrochloric, sulphuric, and nitric acid

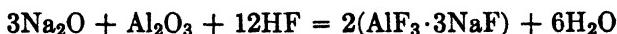
¹⁶ H. Pedersen (Aluminum Company of America), Process of manufacturing aluminum hydroxide, U. S. Patent 1,618,105, Feb. 15, 1927; British Patent 232,930, June 14, 1926.

processes have been developed, all of which seem to possess some special merit.

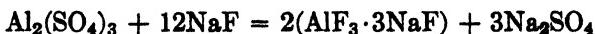
A discussion of these processes cannot be undertaken in a book of this nature. An excellent review of practically all processes is given by Edwards, Frary, and Jeffries and their associates.¹⁷

The Electrolyte. Alumina has so high a melting point, 2,050° C. (3,722° F.), that its use alone as a fused electrolyte is out of the question because it would be difficult to find suitable materials of construction for a cell and the radiation losses would be very high. This matter was a stumbling block in the early electrolytic production of aluminum and was successfully solved by Charles Martin Hall of Oberlin, Ohio. Hall sought some other compound which could be fused at a reasonably low temperature and which would dissolve alumina. Such a compound would act as a solvent and would therefore be required to have a greater electrochemical stability than the alumina, so that the alumina would be decomposed preferentially. He found such a material in cryolite,¹⁸ $\text{AlF}_3 \cdot 3\text{NaF}$. A few months before Hall had applied for his patent, Paul L. Héroult, of Paris, applied for a patent also covering the electrolysis of alumina in cryolite.¹⁹

Cryolite is found in nature in commercial quantities only in Greenland, but it can be prepared synthetically, for which process the fundamental reaction may be represented as



It is also prepared as a by-product in the superphosphate industry:



The solubility of alumina in cryolite is shown in Fig. 81 as determined by Fedotieff and Iljinsky.²⁰ The lowest freezing point, 935° C. (1,715° F.), is obtained at an alumina content of about 15.5 per cent. At 1,000° C. (1,832° F.) about 20 per cent alumina can be dissolved practically, although according to the curve it should dissolve a little more.

Cryolite is a chemical combination of aluminum fluoride and sodium fluoride. Alumina will also dissolve in aluminum fluoride and the

¹⁷ J. D. Edwards, F. C. Frary, and Z. Jeffries, *The Aluminum Industry*, McGraw-Hill Book Company, New York, 1930.

¹⁸ C. M. Hall, Process of reducing aluminum by electrolysis, U. S. Patent 400,766, April 2, 1899.

¹⁹ P. L. Héroult, A process for the electrolytic preparation of aluminum, French Patent 175,711, April 23, 1886 (unpublished).

²⁰ P. P. Fedotieff and W. Iljinsky, *Z. anorg. Chem.*, **80**, 113 (1913).

fluorides of potassium, calcium, or lithium in sufficient quantities to be used as electrolyte. Some of these fluorides may be added to the electrolyte to improve its properties. Cryolite has a low melting point, permits operation at 6 volts, and has a sufficiently low specific gravity to permit pure alumina to sink into the electrolyte.

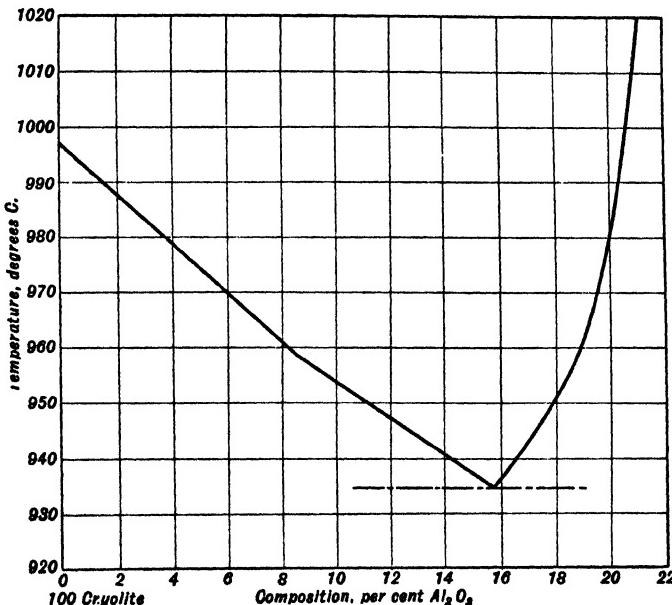


FIG. 81. Freezing-point curve, alumina-cryolite system.

The Electrolysis Cell. The fused electrolyte of alumina and cryolite is very reactive at the operating temperature of 950 to 1,000° C. (1,742 to 1,832° F.). The cell shown diagrammatically in Fig. 82²¹ consists of a strong steel box made of plates from 1 to 2 in. thick. The box has a carbon lining 6 in. or more thick. This carbon lining may be made in two different ways. One is to use a cast-iron form corresponding to the inside dimensions of the cell, and supporting it within the steel shell so that a hot mixture of pulverized coke and coal can be tamped in the space between the two. The whole is then baked in a furnace at about 700° C. (1,292° F.). In the other method the lining is built up out of carbon blocks that have previously been formed and baked. These blocks are cemented together with a mixture of tar, pitch, and ground coke. The lining is very important. It must have sufficient strength to prevent cracking; broken pieces of the lining will float in the bath and,

²¹ Reproduced with permission from J. D. Edwards, F. C. Frary, and Z. Jeffries, *The Aluminum Industry*, McGraw-Hill Book Company, New York, 1930.

may produce local short circuits. Molten aluminum metal may also run into the cracks and make contact with the steel with the result that the aluminum will become contaminated enough to require the cell to be shut down. The lining must also possess good electrical conductivity, for it serves as a conductor to carry the current from the steel shell to the molten aluminum.

The carbon anodes are also made of a mixture of carbon, pitch, and tar, formed in molds or extruded through a die and then baked at a

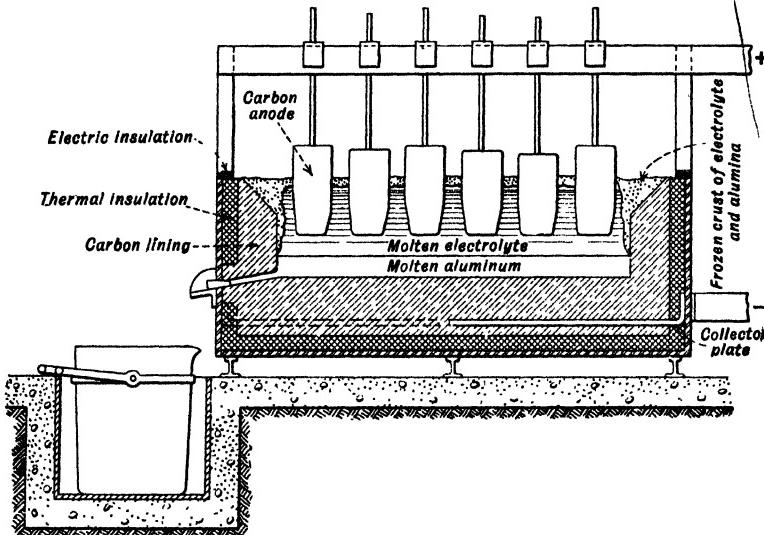


FIG. 82. An aluminum cell in section.²¹

temperature of 1,000° C. (1,832° F.) or above. The carbon used is a petroleum coke or a special low-ash anthracite coke. Ordinary coke contains sufficient silica and iron oxide in its ash to contaminate the aluminum produced.

The anodes are supported by vertical bars of copper, aluminum, or iron from horizontal copper or aluminum bus-bars above the tanks. Each vertical bar, carrying one anode, is clamped to the bus-bar and can be raised or lowered individually. The height of the anodes requires careful adjustment. If the anode is too low, it may make contact with the aluminum and thus carry no load as far as electrolysis is concerned. If it is too high the resistance of the electrolyte will prevent it from carrying its proper load of current.

The size of the cells vary according to the number of amperes the cell is intended to carry. According to Edwards,²² the optimum size of cells

²¹ J. D. Edwards, F. C. Frary, and Z. Jeffries, *op. cit.*, p. 302.

is about 8,000 amp. for the lower limit; 50,000 amp. is now the upper limit. An installation of aluminum cells is shown in Fig. 83.

Cell Operation. A cell in operation contains a lower layer of molten aluminum metal, varying in depth from a fraction of an inch up to 5 in. Above this is a layer of fused electrolyte varying in depth from 6 to 12 in. This consists essentially of molten cryolite in which is dissolved 2

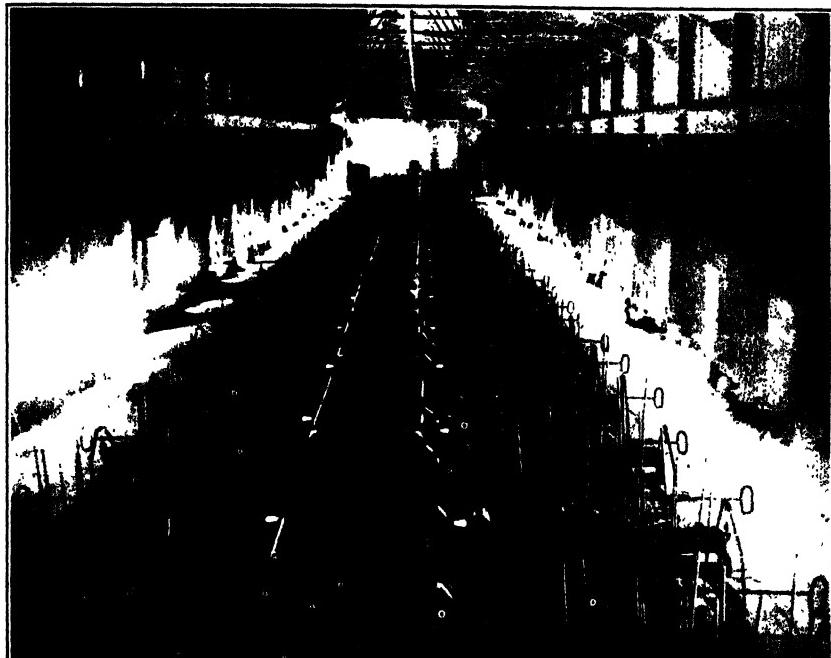


FIG. 83. An installation of aluminum cells. (*Courtesy Aluminum Company of America.*)

to 5 per cent of alumina. Since the density of the aluminum is 2.29 g. per cc. at 1,000° C. (1,832° F.) and that of cryolite is 2.095 g. per cc.,²³ the molten metal will remain at the bottom unless there is violent agitation.

Above the molten electrolyte is a crust of solidified electrolyte. The anodes project through this crust to within 2 to 4 in. from the metal surface. The electrochemical reactions taking place at the electrodes may be represented by the equations



²³ J. D. Edwards and T. A. Moermann, *Chem. & Met. Eng.*, 24, 61 (1921).

During operation, bubbles of carbon monoxide and carbon dioxide gas are given off at the anodes. The evolution of this gas combined with the induction of the current passing through the cell causes continuous agitation. The alumina added to the cell from time to time is heavier than either the fused electrolyte or the aluminum metal, and this stirring action serves to prevent the finely divided alumina from settling at the bottom of the cell underneath the metal before it is dissolved in the cryolite.

The alumina is added periodically, so that between additions the concentration of the alumina in the cryolite decreases, and a point is finally reached when the "anode effect" occurs. The concentration of the alumina is then down to about 2 per cent, although the actual concentration at which this phenomenon occurs depends upon temperature, the composition of the electrolyte, and the current density at the anodes. When anode effect takes place the voltage across the cell rises suddenly from 6 or 7 volts up to 40 or 60 volts. As a signal to the workman an incandescent lamp is connected across the terminals of the cell which glows dimly under normal operation but becomes bright when the voltage rises by reason of the anode effect. The attendant then breaks the crust, on top of which he has previously placed the proper amount of alumina. This addition, together with a vigorous stirring of the electrolyte, causes the anode effect to disappear for several hours.

When the anode effect takes place the carbon anodes are surrounded by a gaseous envelope. The liquid electrolyte does not seem actually to touch or "wet" the anodes so that current passes from the anodes to the electrodes as a multitude of tiny sparks or arcs. The gas evolved at the anodes during this time is carbon monoxide, whereas during normal operation the anode gases contain well above 50 per cent of carbon dioxide. During this time there is also double the normal carbon consumption and several times the heat evolution and power consumption as compared to normal conditions.

The formation of metal fog or clouds is a common phenomenon. Metallic aluminum in extremely fine particles becomes suspended in the electrolyte. Because of the circulation of the electrolyte caused by the electromagnetic forces acting on it, some of the metal fog comes in contact with the anodes where it is reoxidized to alumina resulting in a lower current efficiency.

During normal operation the voltage drop per cell including that of the connections varies between 5 and 7 volts. Forty to 100 cells are connected in series requiring a line e.m.f. from 200 to 600 volts, and each line of cells will take from 8,000 to 30,000 amp.

The power required per pound of aluminum is generally between 10 and 12 kw-hr., and there is an anode carbon consumption of 0.6 to 0.8 lb. per pound of aluminum. The current efficiency varies between 75 and 90 per cent, but the energy efficiency has not been determined accurately owing to lack of information on the decomposition potential of alumina.

Every 1 to 3 days the aluminum collected in the bottom of the cells is tapped into a tapping ladle from which it is transferred to a larger pouring ladle, skimmed with a perforated skimmer, and poured into molds having a capacity of 50 lb. each. In some plants the liquid metal from the ladles is poured into a "holding furnace" so that the metal from many cells is blended before it is cast into molds.

Aluminum Refining

Aluminum produced electrolytically by the Hall process seldom has a purity higher than 99.7 per cent. It cannot be refined electrolytically from aqueous solutions, and organic solvents are expensive and have high resistances. An electrolytic cell using a fused electrolyte has been developed by William Hoopes in cooperation with the research staff of the Aluminum Company of America, using a three-liquid-layer cell ²⁴ based on a patent by Hoopes in 1901. The new cell ²⁵ is illustrated in cross-section in Fig. 84. The cell in some respects is constructed similarly to the aluminum reduction cell. The top cylindrical electrodes, however, are negative, and the carbon lining is positive. Resting on the carbon lining on the bottom of the cell is the aluminum to be refined in the form of a copper-aluminum alloy, low in iron and titanium (they raise the freezing point of the alloy), and containing enough silicon to lower the freezing point sufficiently to permit it to remain adequately mobile even when the aluminum content has been largely reduced. Above the molten anode is a layer of fused electrolyte consisting of a mixture of cryolite, aluminum fluoride, barium fluoride, and alumina. Floating on this is the molten refined aluminum, serving as cathode. The densities of the three liquid layers from the top down, at 950° C. (1,742° F.), are about 2.3, 2.6, and 2.8 g. per cc., respectively.

To start the cell, a layer of molten electrolyte several inches thick is poured into the cell, the graphite connectors are lowered to dip into the electrolyte, and the full-load current is then turned on. A layer

²⁴ F. C. Frary, *Trans. Am. Electrochem. Soc.*, 47, 275 (1925).

²⁵ W. Hoopes (Aluminum Company of America), Cell for electrolytic refining or separating process, U. S. Patent 1,534,320, April 21, 1925.

of molten anode alloy containing aluminum and about 25 per cent copper is slowly poured into the cell, where it sinks to the bottom. A layer of molten aluminum is carefully poured on the surface of the electrolyte. The graphite connectors are readjusted to the proper height, and a crust of electrolyte rich in alumina, and practically non-conducting,

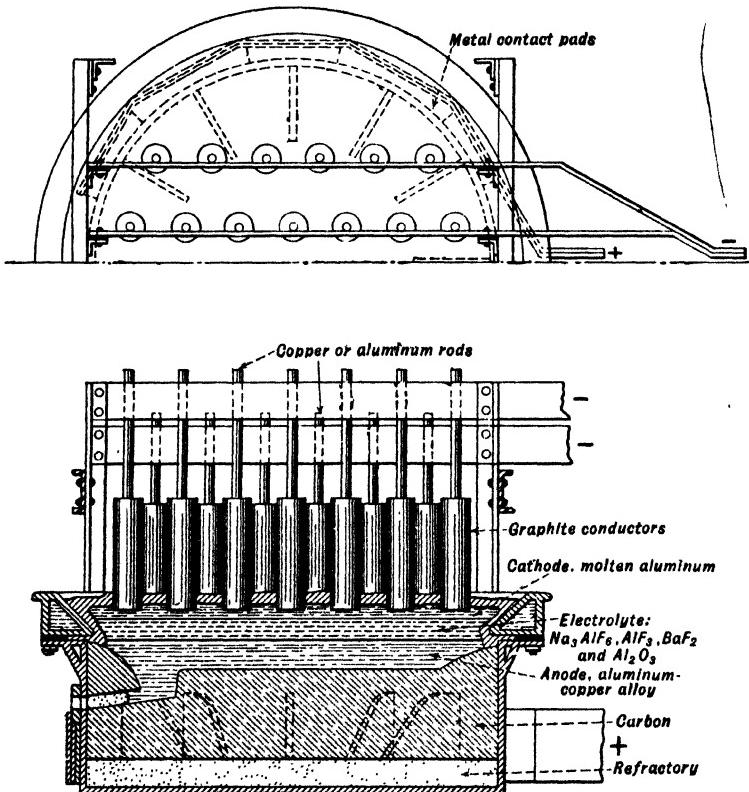


Fig. 84. Aluminum refining cell.

soon forms on the sides and top; in several hours the cell is in normal operation.

Periodically the aluminum removed from the anode must be replaced. The proper amount of impure molten aluminum is poured into a suitable crucible and is placed in a hole in the floor in front of the anode tap hole. The current is shut off, the tap hole opened, and the anode alloy tapped into the crucible of molten aluminum, thus producing an alloy relatively rich in aluminum. This alloy is poured into the cell beneath the fused electrolyte through a carbon-lined funnel extending

into the anode alloy layer. A tap hole in the top section of the cell permits removal of the pure cathode aluminum.

The cell operates at 5 to 7 volts at about 20,000 amp. The average purity of the metal is about 99.80 per cent, and metal as pure as 99.99 per cent has been produced.

BERYLLIUM

Beryllium is the lightest known of the more inert metals, having a specific gravity of 1.85; it is therefore about two-thirds as heavy as aluminum, and but slightly heavier than magnesium. It was discovered by Wöhler,²⁶ who reduced its chloride with metallic calcium. It can also be reduced from the chloride with sodium. On account of the difficulties involved in its reduction it remained a laboratory curiosity for nearly a century.

Beryllium resembles magnesium in appearance and chemical properties, but physically it is a very hard metal and will scratch glass easily. It melts at 1,280° C. (2,336° F.). It is neither malleable (unless pure) nor ductile, and up to the present time no thin sheets, ribbon, or wire have been made.²⁷ It will take a high polish that will not tarnish in air.

The Ore. Beryllium is found in a large number of minerals widely distributed throughout the world. However, for the commercial production of beryllium, only the mineral beryl is used. Beryl is a beryllium-alumina-silicate having the chemical formula $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. The beryllium content of the pure mineral is 5 per cent, but the beryl used in metallurgy has a beryllium content of about 4 per cent. The mineral is widely distributed; in the United States it is found in New Hampshire as giant crystals in granite, and in Connecticut mixed with feldspar. It is also found in appreciable quantities in Massachusetts, North and South Carolina, and South Dakota.²⁸

Electrolysis, Chloride Process. A process has been developed by the Beryllium Products Corporation, New York, formerly the Beryllium Development Corporation, in which the fused chloride is electrolyzed, the metal being obtained in flake form. The beryllium oxide, BeO , is converted to the anhydrous chloride by heating it with carbon in an atmosphere of either chlorine or chlorine and carbon tetrachloride, or with phosgene, moisture and air being excluded from the chlorination chamber. The beryllium chloride, BeCl_2 , sublimes in the colder portions of the chamber.

²⁶ F. Wöhler, *Ann. Physik*, **18**, 577 (1828).

²⁷ A. C. Vivian, *Trans. Faraday Soc.*, **22**, 211 (1926).

²⁸ J. S. Negru, *Chem. & Met. Eng.*, **21**, 353 (1919).

The electrolyte generally consists of a mixture of beryllium chloride and a large amount of sodium chloride: about 25 kg. of sodium chloride to 5 kg. of beryllium chloride. Electrolysis is conducted in a metal pot serving as cathode. The metal pot is preferably of nichrome or a chromium-iron alloy containing 20 per cent chromium, and it is just large enough to hold the charge and a graphite or carbon anode.

To start the electrolysis, the pot containing only the sodium chloride is heated until the salt begins to melt. Hydrogen or some other inert gas is then introduced to prevent the oxidation of the beryllium metal formed later, and the beryllium chloride is slowly added, the temperature being maintained at about 725° C. (1,337° F.). During the course of the electrolysis, as the beryllium chloride content decreases, the temperature is raised about 100° C.

At the start of the electrolysis the current consumed is about 600 amp., at 5 to 8 volts; toward the end, the current is gradually reduced.

At the end of the run the beryllium in flake form is found mixed with the undecomposed electrolyte, the fused salt protecting the metal from oxidation. The mass is transferred to a leaching tank, and the salt is leached away with cold water. The metal is then washed in alcohol and dried.

The flakes of metal cannot be melted directly in the atmosphere, for the metal oxidizes easily and the oxide film prevents the particles from coalescing. The flakes are formed into small rods or discs by being pressed in steel dies under a pressure of several tons. These are then heated in a closed crucible to a temperature of 1,300 to 1,450° C. (2,372 to 2,642° F.) with fused barium chloride or a mixture of 90 per cent barium chloride and 10 per cent barium fluoride. The fluoride dissolves the oxide film on the beryllium particles, thus forming a molten mass of bright metal which on cooling forms a solid coherent ingot.

Electrolysis, Oxyfluoride Process. In Germany a process has been developed in which barium fluoride, BaF_2 , is used as the fused electrolyte in the production of metallic beryllium. The process has been described by Stock²⁹ and by Rimbach and Michel.³⁰

To prepare a suitable salt for electrolysis, the beryl is sintered with sodium silicofluoride; the beryllium sodium fluoride formed is dissolved in water. Any iron that has dissolved is precipitated by blowing air through the solution. The solution is then treated with calcium hydroxide, producing a precipitate of calcium fluoride and beryllium hydroxide.

²⁹ A. Stock, *Trans. Electrochem. Soc.*, **61**, 255 (1932).

³⁰ R. Rimbach and A. J. Michel, Tr., *Beryllium and Its Alloys*, The Chemical Catalog Company, New York, 1932. Issued by the Central Committee on Scientific Research of the Siemens Company, Berlin, 1929.

The beryllium hydroxide is separated as a water-soluble fluoride by treating the precipitate with hydrofluoric acid. When this solution is evaporated, a residue is obtained consisting of beryllium oxyfluoride, $5\text{BeF}_2 \cdot 2\text{BeO}$, which contains 20 to 23 per cent of beryllium. About two-thirds of the beryllium in the beryl is converted into the electrolyte salt.

The beryllium oxyfluoride is mixed with an equal amount of barium

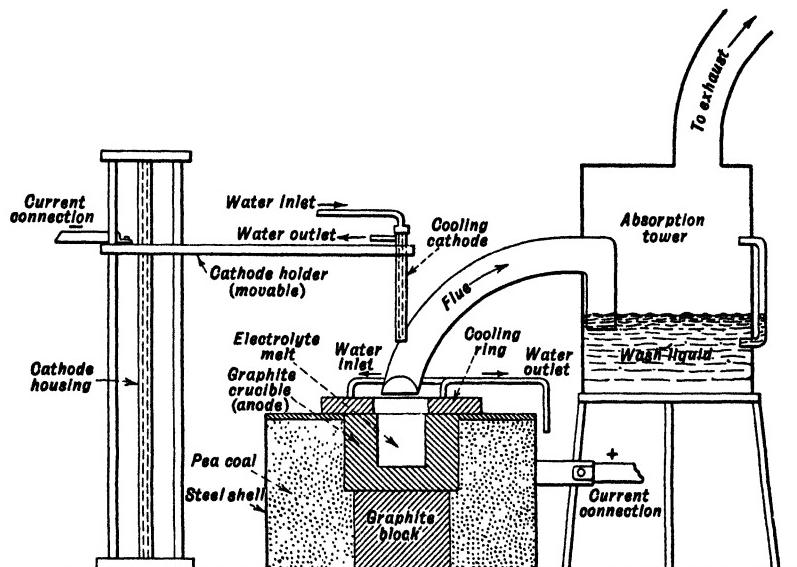


FIG. 85. Beryllium cell, oxyfluoride process.

fluoride for electrolysis. Any iron or aluminum in the bath appears in the beryllium.

The cell is shown in section in Fig. 85. The graphite crucible, which serves as cell and anode, is brought up to heat by filling it with granular coke and pressing a graphite electrode down on this. A sufficiently large current is passed through the mass to bring the crucible to red heat. The coke is then removed from the crucible, and any fine particles of coke are blown out with compressed air. A small amount of a low-melting mixture of sodium fluoride and beryllium fluoride is placed in the cell, and electrolysis is started by introduction of the water-cooled iron cathode. The use of sodium fluoride, which does not form a stable electrolyte, is restricted as much as possible. The current density is then increased, barium fluoride and beryllium oxyfluoride are added to the cell, and the temperature is raised to $1,400^\circ\text{C}$. ($2,552^\circ\text{F}$.). The first cathode, now coated with much fused salt and little beryllium, is re-

moved and a new one is introduced, after which the electrolysis proceeds evenly. Beryllium removed by electrolysis and lost by volatilization of the electrolyte is made up by the addition of beryllium oxyfluoride. A little barium fluoride is also added from time to time.

Provision is made to recover and return to the bath the large amounts of volatilized fluorides. They are recovered in a lead scrubber where barium beryllium fluoride, BaBeF_4 , settles to the bottom and beryllium oxyfluoride goes into solution and is recovered by evaporation. Noxious anode fumes containing large amounts of carbon fluoride are eliminated through the exhauste. A water-cooled cover prolongs the life of the Acheson graphite crucible.

During the course of the electrolysis the cathode is slowly raised out of the bath so that there is only a short end of cathode in the bath. The beryllium metal deposits in the form of a thick rod 30 cm. or more in length. The operation of the cell is continued for 18 to 24 hr. The metal obtained analyzes 0.3 per cent iron, 0.07 per cent aluminum, and 0.04 per cent carbon. The current efficiency amounts to 75 to 80 per cent, and the metal recovery to about 90 per cent of the beryllium in the fused salt or 60 per cent of the beryllium in the original beryl.

The addition of small amounts of beryllium to copper makes the copper much harder and stronger and produces alloys exceptionally responsive to hardening by heat-treatment. The alloys contain 2 to 2.25 per cent beryllium. The alloys, commonly called beryllium-copper, have high resistance to wear and to fatigue, and are used for making non-sparking tools and non-magnetic springs for instruments.

For making beryllium-copper, however, beryllium is not produced as a separate metal but is introduced as the powdered oxide. Copper, beryllium oxide, BeO , and carbon are ground in a ball mill and fed in small amounts into an electric arc furnace. The beryllium oxide is reduced, and the two metals form an alloy.

Beryllium also imparts heat-treating properties to nickel, cobalt, and iron.

CALCIUM

Calcium as a metal has not attained much commercial importance compared to many of the other metals, although it occurs abundantly in the combined state, forming about 3.5 per cent of the earth's crust. It tarnishes readily in the air, reacts with water, and burns with a brilliant crimson flame to form the oxide.

Metallic calcium is produced by the electrolysis of its fused chloride. One of the difficulties involved is the preparation of pure anhydrous calcium chloride; the ordinary fused variety as used for desiccation

purposes is not dehydrated sufficiently. During the dehydration process, hydrolysis and the formation of insoluble basic salts take place easily. If these reactions take place in the electrolysis cell they cause the bath to thicken, the resistance to increase, and the yield to fall off. The condition of the electrolyte grows worse with use, especially if it is allowed to

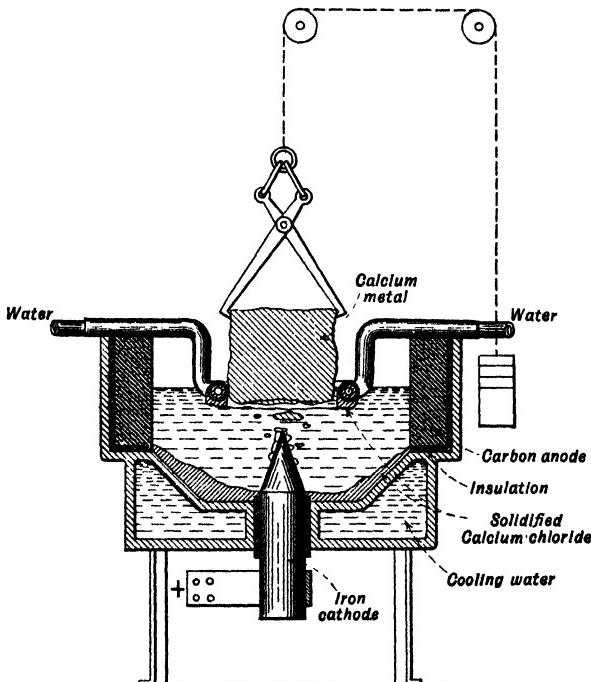


FIG. 86. Calcium cell, Seward and von Kūgelgen.

cool several times. The electrolyte may have to be completely changed from time to time.

A difficulty encountered in the electrolysis of calcium salts was that the metal formed tended to dissolve in the electrolyte, or formed a spongy mass intermixed with electrolyte. This difficulty was overcome by removing the calcium metal from the electrolyte as rapidly as it formed.³¹

One type of cell that has been used with considerable success is illustrated in section in Fig. 86.³² The container is made of cast iron,

³¹ C. Suter and B. Redlich, Process for the electrolytic production of metals of the earthy alkalies, U. S. Patent 813,532, Feb. 27, 1906.

³² G.-O. Seward and F. von Kūgelgen, Producing metals by electrolysis, U. S. Patent 880,760, March 3, 1908.

the upper part of which is lined with an insulating material and then with carbon or graphite serving as anode. The cathode, having a conical shape at its upper end, projects upward through the bottom of the cell and is also insulated from the cast-iron container. Placed above the cathode and concentric with it is a cooling ring, on the bottom of which will collect some solidified electrolyte. The object of this ring with its solid electrolyte is to confine the separated metal rising from the cathode and isolate it from the chlorine separated at the anode.

The electrolyte consists of either calcium chloride alone or calcium chloride mixed with a little calcium fluoride to lower its melting point. Pure calcium chloride melts at 780° C. (1,436° F.). Electrolysis is carried on at a little above the melting point of the electrolyte. The vessel is so adapted that, when filled to the proper level with calcium chloride and receiving a sufficient current to maintain the latter molten, the bottom of the vessel will be protected by a layer of chilled electrolyte. This is accomplished by circulating cold water through the water-jacket in the bottom of the cell.

During operation, calcium metal in the liquid state deposits on the cathode but, being lighter than the electrolyte, immediately rises to the top and is collected within the annular ring. At the start of the electrolysis, care must be exercised to prevent the calcium from burning as it becomes exposed to the air. Soon a cover of solid calcium forms in the ring, and there is enough surface cooling to prevent ignition. As this layer becomes thicker it is gradually raised by a lifting device. The rod or block of calcium thus formed is gradually lifted partly but not fully from the electrolyte.

Another cell for the commercial production of calcium is that developed by Brace,³³ illustrated in Fig. 87. It is designed somewhat like the cells constructed by Goodwin,³⁴ Johnson,³⁵ and Frary³⁶ and his associates, and by Rathenau.³⁷ The cell is about 11 in. in inside diameter and 9 in. deep. The anodes, made of graphite, have a working area of 80 sq. in. The cell will hold a working charge of about 30 lb. of fused electrolyte.

Brace obtained best results with an electrolyte of pure, completely dehydrated calcium chloride. In starting operation of the cell, alter-

³³ P. H. Brace, *Trans. Am. Electrochem. Soc.*, **37**, 465 (1920); *Chem. & Met. Eng.*, **25**, 105 (1921).

³⁴ J. H. Goodwin, *J. Am. Chem. Soc.*, **25**, 873 (1903); **27**, 1403 (1905).

³⁵ A. R. Johnson, *Trans. Am. Electrochem. Soc.*, **18**, 125 (1910).

³⁶ F. C. Frary, H. R. Bicknell, and C. A. Tronson, *ibid.*, **18**, 117 (1910).

³⁷ Rathenau, *Z. Elektrochem.*, **10**, 508 (1904).

nating current is used for producing an arc between the opposite carbon electrodes (which serve as anodes during electrolysis) until sufficient electrolyte is melted to carry the current. When the cell is full of fused electrolyte, direct current is used at a current density of about 515 amp. per sq. in. (80 amp. per sq. cm.) at the iron cathode, requiring a total of about 450 amp. The cathode is continually raised during

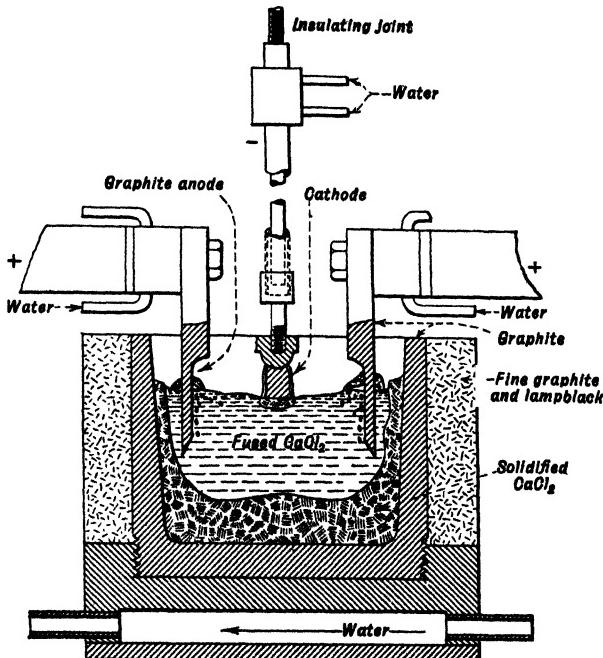


FIG. 87. Brace calcium cell.

operation so that only a small part of the active cathode is immersed in the electrolyte. A crust of electrolyte forms along the sides and bottom of the cell; cooling water in the lower structure of the cell aids in forming the crust. The heating effect of the current keeps the electrolyte in a molten condition at 780 to 800° C. (1,436 to 1,472° F.). The cell requires 25 to 30 volts.

During operation there is a violent evolution of chlorine which carries a fine spray of electrolyte out of the cell. Occasionally the bath must be skimmed, which also causes a loss of electrolyte, and in addition some electrolyte adheres to the calcium as it is withdrawn from the bath. This reduces the yield so that 4 lb. electrolyte is required per pound of metal as compared to 2.76 lb. electrolyte per pound of metal for theoretical yield.

alkaline-earth-metal contents. Approximately three days are required to produce a suitable bearing metal, as for instance, Frary metal containing about 1.6 per cent of barium and 0.4 per cent of calcium. When the proper composition has been reached the current is shut off and the molten alloy is tapped into ladles. The alloy from the various furnaces is mixed in a large kettle for the production of a uniform batch.

Metal fogging, anode effects, and the formation of barium and calcium carbides all combine to reduce the efficiency of the cells.

LITHIUM AND LITHIUM ALLOYS

The electrolytic production of lithium and lithium alloys has been developed to a commercial scale; the process has been described by Osborg.⁴⁴ A variety of processes have been suggested for the production of lithium metal, but only one, the electrolysis of fused lithium chloride, LiCl, appears to have practical value. If, however, lithium chloride is used alone, the electrolysis is soon brought to a standstill, the amperage falls, the voltage rises, and the electrodeposition of lithium gradually diminishes. But the presence of another alkali halide, e.g., potassium chloride, in the electrolysis bath of lithium chloride tends to eliminate these difficulties to a great extent. The presence of potassium chloride in the lithium chloride offers the further advantage that the electrolysis may be conducted at a lower temperature, for, whereas the melting point of pure lithium chloride is approximately 610° C. (1,130° F.), a mixture of equal parts by weight of lithium and potassium chloride has a melting point of about 450° C. (842° F.). The melting point of lithium is about 186° C. (367° F.). The use of potassium chloride was first suggested by Guntz,⁴⁵ and lithium has been produced with the aid of that salt ever since and is used in the present-day commercial units operating continuously and with a high yield. The lithium and potassium chlorides used should be pure and free from moisture.

It is possible to prepare lithium in cells used for the production of sodium, but the current efficiency is relatively low, approximately 65 per cent, while the lithium yield, computed on the basis of lithium chloride used, is about 90 to 92 per cent. In continuous cells now in operation, the current efficiency is over 90 per cent and the metal yield on the basis of lithium chloride input is above 95 per cent. The lithium metal produced is above 99.5 per cent pure. Details of cell construction and operating details are not available.

⁴⁴ H. Osborg, *Trans. Electrochem. Soc.*, **66**, 91 (1934), and *Monograph on Lithium*, The Electrochemical Society, Inc., Columbia University, New York, 1935.

⁴⁵ Guntz, *Compt. rend.*, **117**, 732 (1893).

Of probably equal importance with lithium production is the direct electrolytic production of lithium alloys. If an attempt is made to alloy lithium with metals like iron and nickel by adding the lithium to the molten metal, the lithium on account of its lightness will tend to float to the surface where it burns or vaporizes with consequent loss of the metal. Osborg⁴⁶ has developed processes for producing such alloys electrolytically. For alloys with calcium and other metals of the alkaline-earth family, the alloy is produced in predetermined selected proportions by the electrolysis of a mixed fused salt. For instance, in a cell operating on a commercial scale, the fused bath initially had a composition of 14.5 per cent calcium chloride, 15.5 per cent potassium chloride, and 70 per cent lithium chloride, making a total charge of 112 lb. The current densities were 0.65 amp. per sq. cm. at the anode and 3.75 amp. per sq. cm. at the cathode. The cell operated at 1,900 amp. and at 9.8 volts. Approximately every hour a salt mixture consisting of about 885 g. calcium chloride and 1,800 g. lithium chloride was charged into the bath. The alloy produced contained on the average 50 per cent calcium and 50 per cent lithium.

If a cathode is employed which has an ability to combine with the lithium alloy, an alloy is produced directly on the cathode. For instance, a bath may contain calcium, sodium, and lithium chlorides in such proportions as to produce an alloy with a lead cathode which will contain 0.04 per cent lithium, 0.6 per cent sodium, and 0.7 per cent calcium, the remainder lead. The lead-alloy cathode may then be melted and cast into pigs to be used as a bearing alloy.

It is also possible to use a molten lead cathode at the bottom of the cell in the same manner that mercury is used in the production of sodium and sodium hydroxide.

If an alloy is desired containing lithium and a heavy metal with a relatively high melting point, a cell is prepared as shown in Fig. 88. If an alloy of nickel and lithium is desired, anodes of nickel and graphite are connected in parallel, the nickel anodes about 10 to 25 mm. in diameter being placed in the corners of the cell as shown. If 1,550 amp. is passed through the graphite anode and 1,480 amp. through the nickel anodes, the nickel alloy will contain about 20 per cent lithium. If the current through the graphite is 1,550 amp. and that through the nickel 600 amp., the nickel alloy will contain about 40 per cent lithium.

Lithium is a member of the alkali family. Its specific gravity is 0.534, and it is the lightest of all solid bodies. It reacts slowly with the

⁴⁶ H. Osborg, Lithium alloys and process for producing the same, U. S. Patent 1,869,493, Aug. 2, 1932; and Electrolytic process for producing alloys of lithium, U. S. Patent 1,901,407, March 14, 1933.

air and preferably with its nitrogen if sufficient moisture is present to serve as a catalyst to initiate the formation of the nitride, Li_3N . In the presence of an inert atmosphere, such as paraffin vapor, lithium can be handled, melted, and poured at a temperature of about 200° C . (392° F .). Lithium replaces hydrogen quickly in water. At elevated temperatures lithium will combine with hydrogen to form the relatively stable hydride, LiH . In electrolysis of lithium hydride the lithium is deposited on the cathode; the hydrogen is set free at the anode.

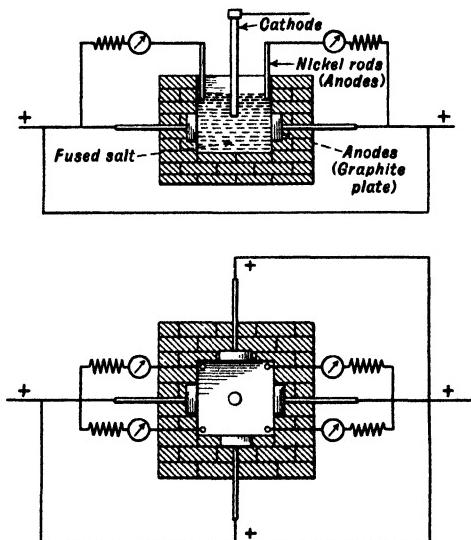


FIG. 88. Diagrammatic views of an Osborg lithium-alloy cell arranged for producing a lithium-nickel alloy.

Cast iron treated with a lithium-calcium alloy becomes more fluid and forms denser castings. The properties of stainless steel of the type 18 per cent chromium and 8 per cent nickel are also improved by the addition of lithium-calcium. "Lithium-copper" is produced by treating the molten copper with approximately 0.025 per cent of lithium alloy, such as 50-50 per cent lithium-calcium. It is free from oxygen, high in density, and high in conductivity. The electrical conductivity of lithium-copper is 101.5 per cent of the International Annealed Copper Standard.

MAGNESIUM

Magnesium as a metal reached the stage of commercial production and utilization only after the beginning of the present century, although it was isolated more than a hundred years ago.

Magnesium metal does not occur in the native state, but in the combined form it is widely distributed and forms about 2.1 per cent of the earth's crust. Gann⁴⁷ points out that magnesium is about 70 times as plentiful as nickel, 200 times as abundant as copper, and of the engineering metals is surpassed in quantity by two metals only—aluminum and iron.

The first substantially pure magnesium metal was produced by Bussy⁴⁸ in 1830, by fusing anhydrous magnesium chloride with potassium. Bunsen, however, prepared the first magnesium electrolytically,⁴⁹ using fused magnesium chloride as the electrolyte. This was later modified so that the dehydrated, naturally occurring mineral, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, was used in place of the pure chloride.

By far the greater part of magnesium produced in the United States is by electrolysis of the fused chloride. In a former process the oxide was used as raw material.⁵⁰ The electrolyte consisted of equal parts of magnesium and barium fluorides, with a little sodium fluoride added as a flux to make the bath fluid at a little below 1,000° C. (1,832° F.). Magnesium oxide was suspended in this fusion, a small amount, about 0.1 per cent, dissolving in the electrolyte. The electrolysis probably decomposed the fluorides, the liberated fluorine at the anode immediately decomposing a corresponding amount of oxide with regeneration of the equivalent amount of magnesium fluoride.

Production of Magnesium Chloride. The magnesium chloride used for electrolysis is obtained in the United States from brine wells and from sea water. The magnesium chloride in the water from both sources is in very small amounts and is mixed with a number of other compounds from which it must be separated.

Magnesium Chloride from Brines. The natural brine from which magnesium chloride is obtained is pumped from wells about 1,300 ft. deep. The brine contains approximately 14 per cent sodium chloride, 9 per cent calcium chloride, 3 per cent magnesium chloride, and 0.15 per cent bromine. After removal of the bromine the brine is treated with a magnesium hydrate slurry to precipitate iron and other impurities. The decanted liquid is evaporated until the sodium chloride has crystallized. The sodium chloride is then removed by filtration, and the calcium and magnesium chlorides in the mother liquor are separated from each

⁴⁷ J. A. Gann, *Trans. Am. Inst. Chem. Engrs.*, **24**, 206 (1930); *Ind. Eng. Chem.*, **22**, 694 (1930).

⁴⁸ A. Bussy, *Pogg. Ann.*, **18**, 140 (1830); *J. Chim. Med.*, **6**, 141 (1830).

⁴⁹ R. Bunsen, *Pogg. Ann.*, **92**, 648 (1854).

⁵⁰ W. G. Harvey, *Trans. Am. Electrochem. Soc.*, **47**, 331 (1925).

other by fractional crystallization. This is described by Gann as follows:

This is made possible by the fact that, under properly controlled composition and temperature conditions, the crystals separating from the complex salt solution may have a different composition from the solids remaining in the mother liquor. In practice this is accomplished by concentrating a solution with a 1 : 3 weight ratio of $MgCl_2$ to $CaCl_2$ whereupon crystals of the double salt "Tachydrite" are formed. The composition of this salt is represented by the formula— $2MgCl_2 \cdot CaCl_2 \cdot 1/2H_2O$. It has a 2 : 1 ratio of $MgCl_2$ to $CaCl_2$, but its crystals are in equilibrium with a mother liquor having a $MgCl_2$ to $CaCl_2$ ratio of 1 : 10. The crystals and liquor are separated in false-bottom tanks. This $CaCl_2$ -rich solution and wash water from the Tachydrite are reworked elsewhere to give $CaCl_2$ and Epsom salts. The Tachydrite crystals are then dissolved in hot water and the solution transferred to a series of crystallizers where substantially pure $MgCl_2 \cdot 6H_2O$ separates, leaving a mother liquor containing $MgCl_2$ and $CaCl_2$ in a ratio of approximately 1 : 1. This solution, together with the $MgCl_2 \cdot 6H_2O$ wash water, contains approximately half of the $MgCl_2$ originally present in the brine and is returned to the process for reworking. In order to facilitate further treatment, the $MgCl_2 \cdot 6H_2O$ crystals are melted in their water of crystallization and the fused mass is flaked on rotating steel drums.

The crystals of magnesium chloride contain 53 per cent water of crystallization. By air-drying on the countercurrent principle it is possible to dry the crystals to a composition corresponding to $MgCl_2 \cdot 2H_2O$, provided that the temperature is regulated carefully to prevent incipient fusion. The remaining molecules of water are removed at a higher temperature in an atmosphere of hydrogen chloride to prevent hydrolysis and the formation of magnesium oxychloride.

Magnesium Chloride from Sea Water. In January, 1941, the Dow Chemical Company at Freeport, Texas, produced the first ingot of any metal to be taken from sea water at any time in the history of the world.^{51, 52} As the sea flows into Freeport Harbor the heavier sea water lies beneath the fresh water on the surface so that the main plant intake is about 30 ft. below the surface. Approximately 300,000,000 gal. per day of sea water is pumped into the plant, part of which is used for magnesium and part for bromine production. After passing through screens to remove trash and refuse the clean sea water flows into a 10-ft. flume to the magnesium operations. In order that the magnesium ions may be removed from the sea water they are precipitated as the hydroxide by treatment with calcium hydroxide, obtained from oyster shells dredged from the bottom of Galveston Bay. The shells are washed and calcined in a gas-fired lime kiln. The lime is slaked and thickened to a slurry and then meets the sea water in a flocculator. The liming operation is carefully controlled to a precise pH adjustment of the mixture.

⁵¹ S. D. Kirkpatrick, *Chem. & Met. Eng.*, **48**, 76, 180 (1941).

⁵² D. H. Killeffer, *A.C.S. News Ed.*, **19**, 1189 (1941).

The magnesium hydroxide floc passes to Dorr thickeners. The clear overflow goes to the waste water canal; the heavy milk-of-magnesia goes to storage tanks. It is then filtered in huge Moore filters, the filter cake of magnesium hydroxide going to rubber-lined steel neutralizing tanks where it is treated with a 10 per cent hydrochloric acid solution to convert the magnesium to the chloride required for the electrolysis.

The hydrochloric acid is made by burning natural gas in the by-product chlorine from the magnesium cells. Additional chlorine is obtained from electrolytic caustic-chlorine cells.

The dilute magnesium chloride solution thus obtained is sprayed into the top of cylindrical brick-lined gas-heated furnaces 20 ft. in diameter and 40 ft. in height. The concentrated solution from these evaporators is filtered to remove solids that have crystallized out in the retention tanks and then passes on to shelf driers. The semi-dried material from the shelves receives its final drying in a gas-fired rotary drier where it is dried to a practically anhydrous condition, ready for the magnesium cell.

The plant has an annual capacity of 18,000,000 lb. of magnesium. Eight hundred tons of sea water are processed to produce one ton of magnesium.

Electrolysis, Continuous Chloride Process. A process has been developed by the Dow Chemical Company, and described by Gann,¹⁴ in which a cell using magnesium chloride as the electrolyte is operated continuously.

The electrolysis cells consist of large rectangular cast-steel pots having a capacity of several tons of molten electrolyte. The steel container serves as cathode; the anode consists of graphite bars. The dehydrated magnesium chloride is fed into the cell either continuously or intermittently, an approximately constant bath level being maintained. Sodium chloride is added from time to time to reduce the melting point and increase the conductivity of the bath. The composition of the bath is approximately 25 per cent magnesium chloride, 60 per cent sodium chloride, and 15 per cent calcium chloride. Exterior heating supplied by a series of stoker-fired furnaces reduces the power consumption by helping to maintain the proper bath temperature.

The magnesium metal produced is lighter than the cell bath and rises to the surface. A thin film of molten salt protects the metal so that it does not burn. The metal is removed daily.

The small percentage of magnesium oxide in the cell feed causes a heavy sludge to form, during the operation of the cell, which settles to the bottom. The purity of the cell feed, the settling of the sludge, and

¹⁴ J. A. Gann, *Am. Inst. Chem. Engrs.*, 24, 206 (1930); *Ind. Eng. Chem.*, 22, 694 (1930).

the floating of the magnesium metal, together with the purifying and washing action of the bath itself, all contribute to produce a metal of such purity that subsequent refining is unnecessary. The average analysis of the magnesium direct from the cells reveals a purity of 99.9 per cent.

An installation of magnesium cells is shown in Fig. 89.

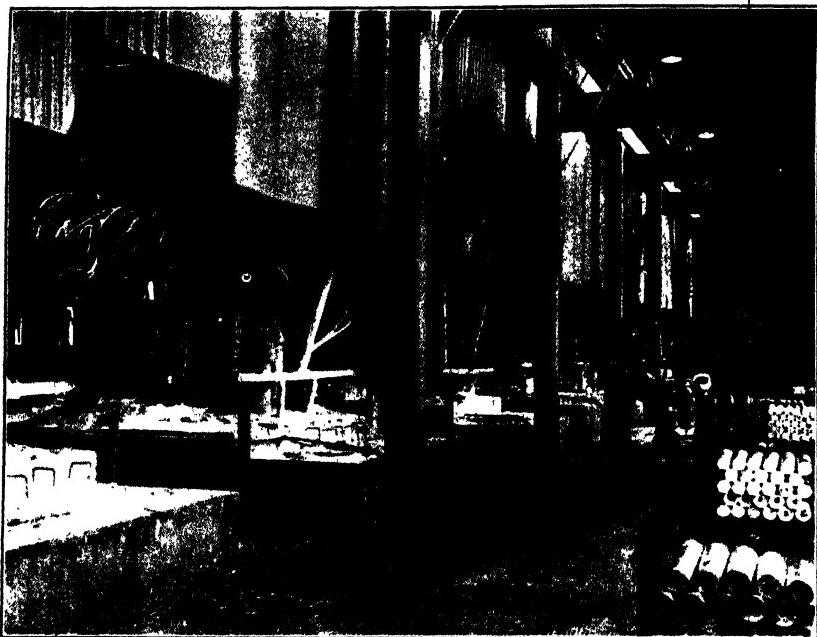


FIG. 89. An installation of magnesium cells. (Courtesy Dow Chemical Company.)

The cells used by the Dow Chemical Company for producing magnesium from sea water are about 6 ft. wide and 12 ft. long. The steel pot serves as cathode; graphite electrodes enter the open tops of the cell. The electrolyte is kept in a molten state at 670 to 730° C. (1,238 to 1,346° F.) by gas-fired furnaces, or it can be heated by electric power alone. The normal operating voltage is 6 to 9 volts; 8 to 10 kw-hr. is required per pound of magnesium. Each cell produces about 1,000 lb. of metal per day.

Electrolysis, Intermittent Chloride Process. Magnesium metal can also be manufactured by an intermittent process, as described by Harvey.⁵⁴ The process has many points in common with the continuous process. The cell, shown in Fig. 90, consists of a cast-steel pot which also

⁵⁴ W. G. Harvey, *Trans. Am. Electrochem. Soc.*, 47, 327 (1925).

serves as cathode. The anode, consisting of graphite about 6 in. in diameter and 24 in. long, is suspended centrally in the fused salt, and is provided with means for varying its height so that it can follow the bath level, which lowers during electrolysis.

The raw material for the bath consists of approximately equal parts of $MgCl_2 \cdot 6H_2O$ and NaCl. The sodium chloride is added to prevent

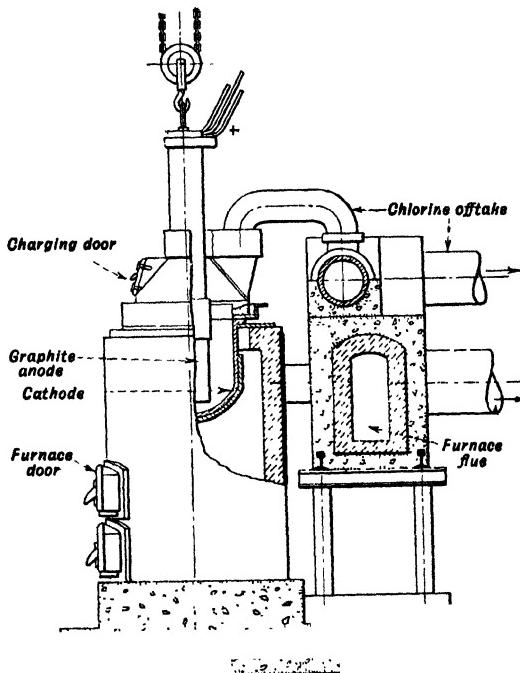


FIG. 90. Magnesium cell, intermittent chloride process.

formation of magnesium oxide during dehydration and fusion. A small amount of ammonium chloride is added to retard decomposition of the magnesium chloride. The mixed salts are dehydrated by carefully heating with stirring in iron pots over a slow fire until five or six molecules of water are removed. The salts are then quickly transferred to a hot, quick fire where the final water is removed. The mixed salts melt to a fairly clear fusion containing 10 per cent magnesium oxide. The mixture has a melting point of about $620^{\circ} C.$ ($1,148^{\circ} F.$). The temperature of the electrolyte is maintained partly by its resistance to the current and partly by a slow coal fire under the steel pot. It is possible to maintain the proper operating temperature of 675 to $725^{\circ} C.$ ($1,247$ to $1,337^{\circ} F.$)

by the heating produced by the current only, but the voltage rises from an average of 7.6 to 11 volts.

The magnesium, being lighter than the electrolyte, floats on the top and is removed hourly by opening the door in the hood and skimming off the metal with a ladle containing small perforations which allow most of the fused salt to drain off but retain the metal. The furnace metal carries about 10 per cent of electrolyte, most of which is removed by further refining or remelting in oil-fired steel pots, but a complete separation is extremely difficult.

It requires 24 hr. to work down a charge. The average current is 2,200 amp. at 6 to 9 volts, which corresponds to a current density of 16 amp. per sq. in. of anode surface. The daily production is about 40 lb. of refined metal per furnace at a current efficiency of 75 per cent. An installation of magnesium cells is shown in Fig. 89.

Ward Cell. Ward⁵⁵ has developed a cell for producing magnesium from magnesium chloride, placing anodes and cathodes close together to reduce the resistance within the cell with a corresponding increase in the energy efficiency. Special means are therefore provided for removing the liberated magnesium from the section of the cell where the chlorine is likely to react with it. The cathodes are placed on opposite sides of the row of anodes as shown in Fig. 91. The droplets of metallic

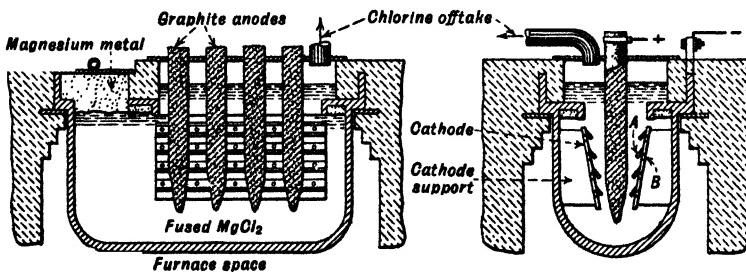


FIG. 91. Ward magnesium cell, using magnesium chloride.

magnesium tend to float upwards but are prevented from doing so directly by the deflectors, A. These deflectors form inverted troughs with the cathode surface and deflect the magnesium through the ports, B, into the inactive space back of the cathode where it is protected from contact with chlorine. The droplets of magnesium then rise and are caught in a channel above, which directs all the magnesium to the reservoir shown at the left.

The cathodes slope toward each other at the bottom; this taper is designed to correspond to the natural wear of the anodes in service.

⁵⁵ L. E. Ward (Dow Chemical Company), Electrolytic apparatus, U. S. Patent 1,921,377, Aug. 8, 1933.

The anodes are said to wear more uniformly and less rapidly, and do not "neck down" and break off as when wear is less uniform. No operating data of the cell are available.

Foundry of the Metal. Molten magnesium reacts readily with oxygen and nitrogen of the air and with moisture. It is therefore necessary to exclude air and moisture from the metal, which is best accomplished by the use of a flux. A suitable flux consists of an anhydrous mixture of magnesium and sodium chlorides similar in composition to the bath used in the electrolysis cell. The major part of the flux settles to the bottom of the melting pot, but a thin film completely envelops the metal. The flux has no chemical action on the magnesium metal but removes non-metallic impurities by causing them to coalesce into a dense, heavy sludge. The charge is puddled with a ladle to produce intimate contact between the metal and the flux. The refined metal is dipped from the pots by the use of bottom-pour ladles equipped with skimming lips and underfeed spouts.

Magnesium may also be purified by a distillation or sublimation process⁵⁶ which is especially suited for impure metal and scrap recovery. It is carried out under reduced pressure at temperatures below the boiling point of magnesium. Under a pressure of 2 mm. of mercury the metal sublimes. Impure metal of 90 per cent magnesium can be converted to 99.99 per cent magnesium. The method can be made continuous by charging metal through a vacuum lock arrangement and tapping off the condensed purified liquid metal into molds within a vacuum chamber.

Magnesium metal is used in military pyrotechnics; the light emitted from the burning metal is very brilliant and has a high actinic value. It is also used for flashlight powders. For either purpose it is in powdered form of 30 to 200 mesh. In the massive or coherent form it is quite stable, and bars have been forged successfully in an open blacksmith forge. It is used as a getter or scavenger reagent in the vacuum-tube industry, where its specific value is due its high chemical affinities at elevated temperatures. Magnesium vapor combines with practically every gas except the rare gases. On account of its high chemical affinity at elevated temperatures it is the preferred scavenger for nickel to remove oxygen and sulphur, for unlike aluminum it does not readily alloy with nickel. It is used in the organic chemical field in the Grignard reaction; many organic compounds owe their existence to reactions in which magnesium metal plays the key role.

Most of the metal is used in alloys as a material of construction in the form of castings or as worked or wrought metal. Dow metal contains

⁵⁶ H. E. Bakken, *Chem. & Met. Eng.*, 36, 345 (1929).

from 4 to 12 per cent aluminum, the rest being magnesium. Large quantities of magnesium alloys are used in airplane construction.

SODIUM

Sodium metal was first isolated by Sir Humphry Davy in 1807 by electrolysis of fused sodium hydroxide. It was prepared commercially for many years after, however, by a distillation process starting with a mixture of sodium carbonate, charcoal, and lime. Later Castner improved the output efficiency by substituting the lower-melting caustic soda for the carbonate and replacing the charcoal by the more active iron carbide. About 50 years after its isolation it was used to reduce alumina in the manufacture of aluminum, and, for more than 30 years after, its history was closely linked with that of aluminum. After the development of Hall's electrolytic process for preparation of aluminum, the demand for sodium metal dwindled to small proportions for a number of years.

Since the end of the first decade of the present century the demand for sodium has steadily increased. The domestic output in respect to annual tonnage produced is far greater than that of mercury, magnesium, molybdenum, bismuth, cadmium, cobalt, gold, or silver.⁵⁷

Sodium metal is used principally in the preparation of sodium cyanide, sodium peroxide, tetraethyl lead, and vat dye indigo; as an important reducing agent in organic synthesis; as a deoxidizing agent in light alloys; and as a reducing agent in the preparation of some of the rarer metals and in bearing alloys. It also has a number of minor uses. It has been proposed as a substitute for copper for electrical conductors. Its conductance is three times that of an equal weight of copper, and its cost on a conductance basis is lower than that of any other metal. For such use the sodium would have to be encased in a holder such as a thin-walled tube of some non-magnetic alloy steel.

Sodium metal is marketed in 1-oz., 1-lb., and 5-lb. air-tight tins, in 12½-lb. bricks and 280-lb. drums.

Sodium is produced by the electrolysis of either sodium hydroxide or sodium chloride. Castner in 1890 developed an electrolysis cell for the production of sodium, using fused caustic. This electrolytic process was a great improvement over the former commercial method, also developed by Castner, in which molten caustic was reduced by a mixture of carbon and iron. Castner's electrolytic process, using sodium hydroxide as a fused electrolyte, was the sole commercial method for the manufacture of sodium for many years. The industry, however,

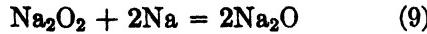
⁵⁷ P. M. Tyler, *U. S. Bur. Mines Circ.*, 6579, 1932.

was much interested in using sodium chloride as the fused electrolyte on account of its lower cost, but, owing to its relatively high melting point and the operating difficulties that this introduced, it required many years of research before sodium chloride found commercial application in the preparation of sodium.

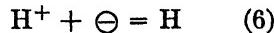
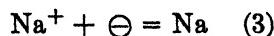
Sodium from Sodium Hydroxide. When fused sodium hydroxide is electrolyzed between unattackable electrodes, Na^+ ions are discharged at the cathode and OH^- ions at the anode. Each two hydroxyls discharged at the anode combine to form water and oxygen, equation 4. The water formed will itself be decomposed electrolytically to liberate hydrogen at the cathode, equation 6, and more hydroxyl at the anode. The liberated sodium is somewhat soluble in the fused caustic, and at temperatures appreciably above its melting point a considerable amount will diffuse to the anode where part of it will combine with water to form sodium hydroxide and hydrogen, equation 7, so that hydrogen will be liberated at the anode. Some of the dissolved sodium at the anode will combine with oxygen to form sodium peroxide, equation 8, which in turn combines with more sodium to form sodium oxide, equation 9. The sodium oxide combines with water to form sodium hydroxide, equation 10. In addition, some of the sodium dissolved in the electrolyte at the anode will give up electrons and become sodium ions, equation 11. These reactions are represented by the following equations:



ANODE (+)



CATHODE (-)



All the reactions indicated above except those represented by equations 2 and 3 reduce the yield of sodium so that at best the current yield is only about 45 per cent; and, if the temperature is about 20 to 25° C. above the melting point of the caustic electrolyte, the rate of recombination of the sodium is about equal to that of its liberation so that no metal is produced.

Castner Cell. For many years sodium was chiefly produced by Castner's process,⁵⁸ using fused sodium hydroxide as the electrolyte. The process is still in practice,⁵⁹ although it is superseded in part by the more difficult but cheaper fused sodium chloride process. The cell, Fig. 92, consists of an iron container surrounded by brickwork so arranged that the caustic in the container can be heated by gas. The cathode, consisting of iron, copper, or nickel, enters the cell from the bottom through a narrow extension of the container. This extension

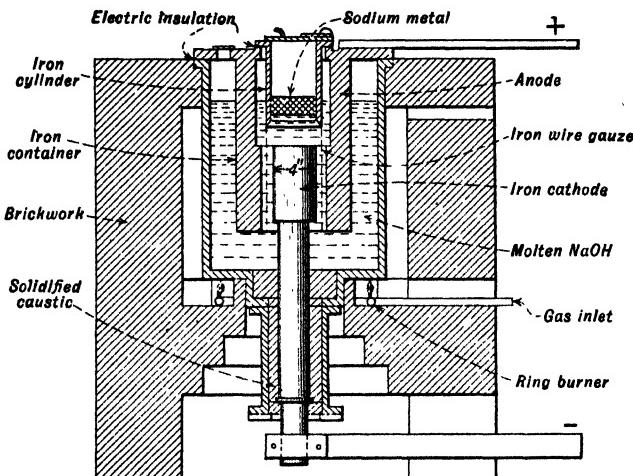


FIG. 92. Castner sodium cell, using sodium hydroxide.

is filled with frozen caustic which holds the cathode rigidly in place. A cylindrical collector for sodium is supported directly above the cathode. Supported from the lower end of the collector is another cylinder, but made of iron-wire gauze which completely surrounds the upper or active part of the cathode and serves as a diaphragm. The anode consists of a cast-iron cylinder and completely surrounds the sodium collector and the gauze, with a narrow annular space between. The anode may also consist of bars suspended from the cover.

In the operation of the cell the sodium is deposited on the cathode, but being lighter than the fused caustic it immediately rises and is caught in the collector above. The iron gauze prevents sodium particles from passing to the anode. A cover on the collector permits removal of the sodium with a ladle.

⁵⁸ H. Y. Castner, Process for manufacturing sodium and potassium, U. S. Patent 452,030, May 12, 1891.

⁵⁹ C. Fink, *A.C.S. News Ed.*, 19, 196 (1941).

The cells are about 18 in. in diameter and 24 in. deep, and they hold about 250 lb. of molten caustic. It is desirable that the caustic be pure and dry. Moisture can be removed by the addition of metallic sodium. The presence of sodium chloride is objectionable, for it attacks the iron parts of the cell and thus fouls the electrolyte. Sodium hydroxide produced electrolytically in mercury cells would therefore appear to be preferable for use as the raw material.

The operating temperature should not be much above the melting point of the caustic. The melting point of pure sodium hydroxide is 318° C. (604° F.), but impurities may reduce this to 300° C. (586° F.), so that the usual operating temperature is about 310 to 320° C. (590 to 608° F.). At about 25° C. above the melting point of the caustic the rate of diffusion of the liberated sodium in the electrolyte is so great that the recombination of the sodium is about equal to the rate of decomposition of the hydroxide, and the yield is practically zero. At a temperature of 5° C. above the melting point of sodium hydroxide, the yield can be made equal to the theoretical.

Dissolved and fine particles of sodium small enough to pass through the screen tend to diffuse toward the anode, where they react with the atmospheric or anodic oxygen, equation 8, to cause small explosions with a consequent loss in yield. The gauze screen surrounding the cathode is designed to prevent this, but if the meshes are too fine the gauze acts as a bipolar electrode. Screens of non-conducting material like alumina or sodium aluminite have been proposed, but they do not appear to be practicable. This discharge of the hydroxyl at the anode produces water and oxygen, equations 2 and 4; and some of the diffused sodium reaching the anode combines with the water to form hydrogen, equation 7. The hydrogen and oxygen combine, producing small explosions. Hydrogen is normally liberated at the cathode, equation 6, where it combines with atmospheric oxygen, also causing explosions. Therefore a number of small explosions will take place within a cell in operation, but by carefully controlled conditions they may be greatly reduced. Operation at a low temperature and a relatively low current density reduces convection currents with the result that fewer sodium particles reach the anode.

The operating voltage is about 5 volts, and the current efficiency about 40 per cent. The decomposition potential of sodium hydroxide being taken as 2.25⁶⁰ at 340° C. (644° F.), the energy efficiency can be calculated to be 18 per cent.

⁶⁰ A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, p. 502, Edward Arnold and Company, London, 1924.

Sodium from Sodium Chloride. Sodium chloride has the advantage over sodium hydroxide as a source of sodium in that it is a cheaper raw material and chlorine is obtained as a by-product. The disadvantage of sodium chloride lies in its higher melting point of 805° C. (1,481° F.) for the pure material as compared to 318° C. (604° F.) for the hydroxide. The high operating temperature introduces the problem of obtaining suitable materials for construction of the cell. Sodium metal if exposed to the atmosphere at 600° C. (1,112° F.) burns readily, so that the cell must be constructed to protect the metal from oxidation.

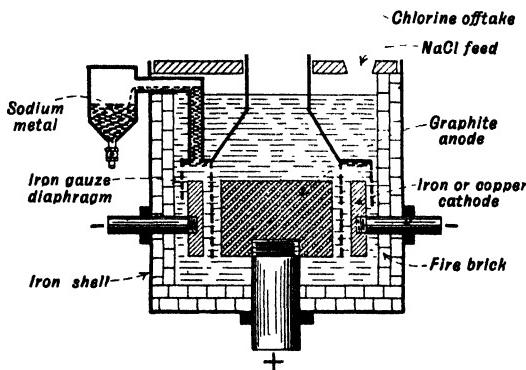


FIG. 93. Downs sodium cell, using sodium chloride.

In order to lower the melting point of the salt, a second compound is added; for instance, Smith and Veazey⁶¹ found that a mixture of 35.6 parts sodium chloride and 64.4 parts sodium carbonate by weight has a melting point of 600° C. (1,112° F.) and upon electrolysis in a Castner cell produces metallic sodium.

Downs Cell. Downs⁶² has designed a cell which has been used successfully for the production of metallic sodium from fused sodium chloride. The cell is shown diagrammatically in Fig. 93. The container consists of an iron shell lined with firebrick. The anode consists of a block of graphite or carbon, the anode lead coming in through the bottom of the cell. Surrounding the anode is an annular cathode made of iron or copper, and between the anode and cathode is an iron gauze diaphragm. The diaphragm terminates at the top in a chlorine-collecting dome made of a ceramic material such as stoneware. The sodium

⁶¹ A. W. Smith and W. R. Veazey (Dow Chemical Company), Method of making metallic sodium, U. S. Patent 1,334,179, March 16, 1920.

⁶² J. C. Downs (Roessler and Hasslacher Chemical Company), Electrolytic process and cell, U. S. Patent 1,501,756, July 15, 1924.

liberated at the cathode is collected, gradually filling the riser pipe and then overflowing into the sodium collector. When the cell is operating properly a continuous stream of molten sodium flows into the collector. Electrolyte can be fed into the cell through an opening in the cover.

The cell operates at about 600° C. (1,112° F.). The temperature of the cell is maintained by the current, and the current efficiency is under 80 per cent. The energy consumption is about 15 kw-hr. per kg.

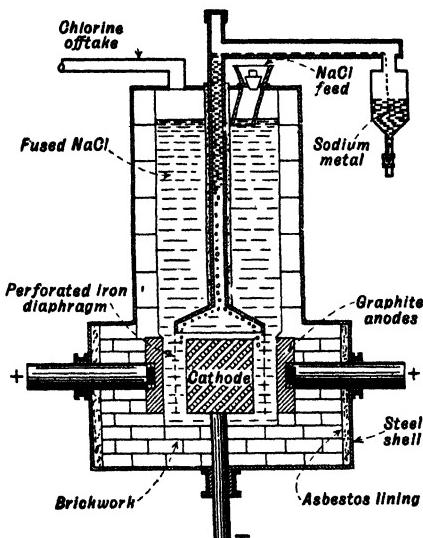


FIG. 94. McNitt sodium cell, using sodium chloride.

A special feature of the cell is that the chlorine produced is dry and therefore requires no drying before being compressed for packaging.

Other Cells for Producing Sodium. *The McNitt cell*⁶³ shown in Fig. 94 was the predecessor of the Downs cell. One of its chief differences lies in the interchange of the electrodes.

The Acker cell,⁶⁴ Fig. 95, is of historic interest because it was the first type of cell to produce sodium from sodium chloride successfully. The sodium, however, existed in the cell in the uncombined state for only a short time as a sodium-lead alloy and was recovered from the lead by steam, in the form of sodium hydroxide.

The Ashcroft cell,⁶⁵ Fig. 96, also using sodium chloride, was at one time in large-scale operation in Norway. The cell consisted of two comp-

⁶³ R. J. McNitt, Method for reducing metals, U. S. Patent 1,214,808, Feb. 6, 1917.

⁶⁴ C. E. Acker, *Trans. Am. Electrochem. Soc.*, 1, 165 (1902).

⁶⁵ E. A. Ashcroft, *ibid.*, 9, 123 (1906).

ments: the decomposing compartment, in which the sodium chloride was electrolyzed and the liberated sodium was dissolved in a melted lead cathode; and a producing compartment, in which the fused lead-sodium

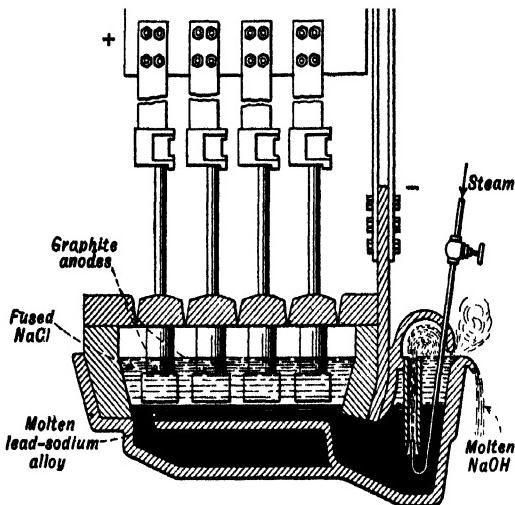


FIG. 95. Acker sodium cell, using sodium chloride.

alloy served as anode. The sodium passed into the fused sodium hydroxide electrolyte and plated out on a spherically shaped nickel cathode.

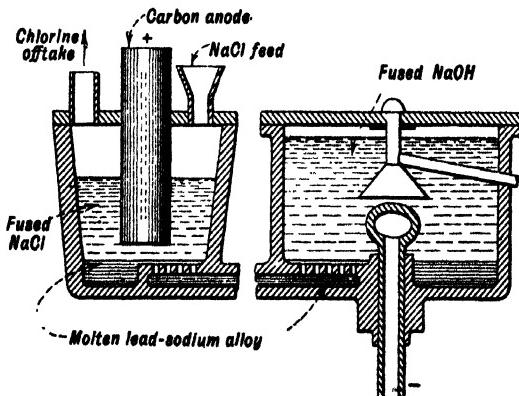


FIG. 96. Ashcroft sodium cell, using sodium chloride.

A hood above the cathode collected the sodium, which is lighter than the fused caustic, and a conducting pipe led the sodium out of the cell in a continuous stream.

CHAPTER X

THE ELECTROLYSIS OF ALKALI HALIDES

All the alkali halides can be decomposed by the electrolysis of their aqueous solutions or of their fused salts, but only the electrolysis of sodium chloride and to a much lesser extent of potassium chloride has attained commercial importance. The electrolysis of sodium chloride is a very important electrochemical industry. Unless specifically mentioned otherwise, the discussions in this chapter are limited to the decomposition of sodium chloride in aqueous solutions.

General Theory. When sodium chloride is dissolved in water, the dissociation of the salt liberates Na^+ ions and Cl^- ions while the water contains H^+ ions and OH^- ions. When a salt solution is electrolyzed between unattackable electrodes (such as platinum, carbon, or a carbon anode and an iron cathode), Cl^- ions are discharged at the anode and H^+ ions at the cathode. This will leave Na^+ ions and OH^- ions in the solution to form sodium hydroxide. The electrode reactions can be represented by



The chlorine liberated is sparingly soluble in the electrolyte and unless held in some chemical combination will almost immediately begin to escape as a gas. If the object of the electrolysis is the production of chlorine and sodium hydroxide, the anode and cathode products (chlorine and sodium hydroxide, respectively) are kept separate so that they cannot react with each other. If the object, however, is the production of sodium (or potassium) hypochlorite, NaClO , or chlorate, NaClO_3 , or perchlorate, NaClO_4 , the chlorine and alkali hydroxide are brought into intimate contact so that the two can react.

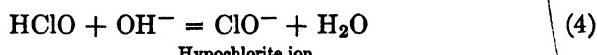
HYPOCHLORITES

When sodium chloride is electrolyzed between unattackable electrodes chlorine and sodium hydroxide are produced; all alkali halides will decompose similarly. Unless special means are employed to keep the

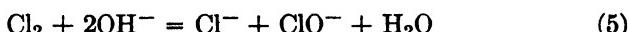
two products separate, they will combine with each other. For chlorine and hydroxyl ions the reaction is



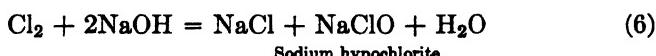
The reaction is reversible, though with chlorine the reaction is very predominately from left to right at equilibrium conditions, but such equilibrium conditions are not reached in a hypochlorite cell, for the hypochlorous acid formed is removed by combination with the sodium hydroxide or, more specifically, with the hydroxyl ions.



By adding equations 3 and 4 the process can be represented by one equation:

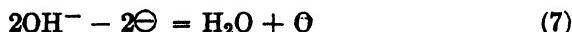


This can be written in the customary form



It will be observed that Na^+ ions do not appear in equation 5, for in the whole process these ions are merely by-standers while their companion negative ions are being changed. It is important to note in equation 6 that of the two chlorine atoms entering into the reaction one reappears in sodium chloride, so that only 50 per cent of the chlorine discharged at the anode is combined as hypochlorite.

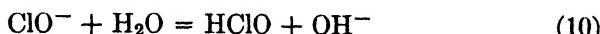
If the above reactions were the only ones taking place it would be possible to electrolyze a sodium or potassium chloride solution until practically all the chloride is converted to hypochlorite, but a number of other reactions prevent this. Not all the hydroxyl ions combine as indicated in equations 3 and 4, but some may migrate and diffuse to the anode and there be discharged:



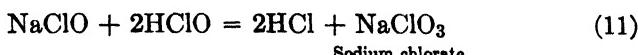
The oxygen escapes at the anode. However, the discharge of OH^- ions is not very pronounced at low temperatures. Furthermore, the sodium hypochlorite is itself dissociated to a considerable degree into Na^+ and ClO^- ions; some of the hypochlorite ions will reach the anode and will there be discharged, and the freed hypochlorite radical will combine with water; this is illustrated in equations 8 and 9:



In practice, neutral brine solutions are used; in the immediate vicinity of the anode, the OH^- concentration is low, but the ClO^- ions formed in the bulk of the electrolyte can migrate easily to the anode region of low OH^- concentration. Hydrolysis can then take place, represented by



Owing to the high concentration of chlorine near the anode, more hypochlorous acid will be present there than in other parts of the electrolyte. This hypochlorous acid reacts with the sodium hypochlorite to form chlorate and hydrochloric acid:



The hydrochloric acid produces more hypochlorous acid:



which helps the reaction represented by equation 11 continually to decompose more hypochlorite; reaction 11 is accelerated at elevated temperatures. At the cathode, hypochlorite is attacked by the hydrogen:



This decomposition takes place at the cathode but can be reduced considerably by the addition of a little potassium chromate, K_2CrO_4 , to the electrolyte; its action appears to be due to the formation of an insoluble coating of chromate around the cathode which prevents the hypochlorite from coming in direct contact with the nascent hydrogen which is liberated directly on the cathode. One use of hypochlorite is for whitening (bleaching) clothes in laundries; the chromate cannot be used for this, for it will itself color the clothes. A high-molecular-weight, non-aromatic organic sulphur compound like Turkey red oil, in the presence of calcium salts, has a similar action; the calcium salt (e.g., calcium chloride) causes hydrated lime to form on the cathode where it acts like a diaphragm just as the film of chromate does; the Turkey red oil forms a diaphragm at the anode and prevents the formation of chlorate.

In addition, the hypochlorite may be decomposed by reactions represented by the following equations:



and



These reactions, which occur in alkaline solutions, take place very slowly so that the hypochlorite solution can be stored for days. However, reac-

tion 15 may proceed quite rapidly if catalysts, such as oxides of cobalt, nickel, copper, iron, or platinum black, are present.

It is not possible, therefore, to continue the electrolysis until a saturated solution of hypochlorite is obtained. Of the various side reactions operating to reduce or limit the yield of hypochlorite, those represented by equations 7, 10, 11, 13, 14, and 15 can be reduced to small importance by proper operating conditions. However, the anodic dis-

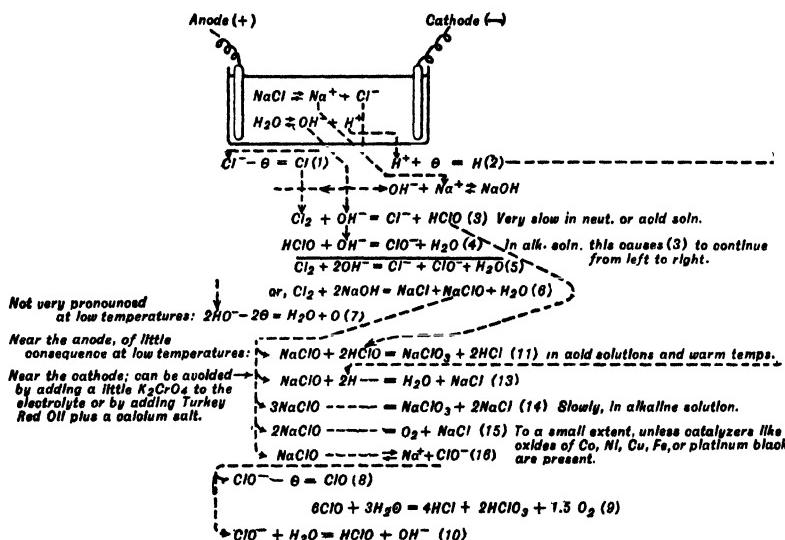


FIG. 97. Primary and secondary reactions when sodium chloride in aqueous solution is decomposed between unattackable electrodes. The equations are numbered the same as in the text.

charge of hypochlorite ions, equations 8 and 9, cannot be so reduced; therefore after a cell has been in operation sufficiently to reach a stationary rate, two-thirds of the current will be spent in producing chlorine, which reacts with the hydroxide giving ClO^- ions, and one-third in the discharge of ClO^- ions.

The above reactions are recapitulated in Fig. 97.

Conditions most favorable for the electrochemical production of hypochlorite are listed below, together with comments on the practicability of producing these conditions.

1. The electrolyte should be neutral, for an acid will produce hypochlorous acid according to equation 12 and this acid will decompose the hypochlorite according to equation 11.
2. The concentration of sodium chloride in the electrolyte should be high. This lowers the resistance of the cell, and the hypochlorite solu-

tion produced will be stronger, for, the higher the sodium chloride concentration, the more easily are the Cl^- ions discharged, and therefore the greater must be the concentration of ClO^- ions before they are discharged.

3. The cell should be designed to permit an undisturbed diffusion layer at the anode; this allows an impoverishment of ClO^- ions at the anode, and therefore their discharge according to equations 8 and 9 will be reduced.

4. The cell should be operated at a low temperature, for the decomposition of sodium hypochlorite by the hypochlorous acid, equation 11, the discharge of OH^- ions, equation 7, and the discharge of ClO^- ions, equation 8, proceed less rapidly at low temperatures. Low-temperature operation requires artificial cooling and is therefore not generally used. The temperature in the cell, however, should not be above 40° C. (105° F.).

5. Potassium chromate, K_2CrO_4 , or Turkey red oil plus calcium chloride may be added to prevent the interaction of the hypochlorite and nascent hydrogen, equation 13. However, if the hypochlorite solution is to be used for bleaching purposes the potassium chromate is objectionable on account of its color.

6. The cell should be operated at a high current density; this produces a higher concentration of hypochlorite. The reason is probably that, the Cl^- ions being discharged faster, the diffusion layer becomes thicker, and as a result fewer ClO^- ions are discharged. A high current density, however, raises the temperature of the cell, and the advantages of operating at low temperatures are lost.

7. Experiment has shown that platinized electrodes yield a higher concentration of sodium hypochlorite than any other electrodes. Prausnitz¹ has succeeded, with the aid of platinum electrodes, in obtaining 100 g. per liter of active chlorine; usual commercial methods yield concentrations very much less than value. On account of their cost, platinum electrodes are not widely used commercially.

Technical Cells for Hypochlorite

Electro Chemical Company Cell. The Electro Chemical Company is the manufacturer of several types of hypochlorite cells that are in common use in America. One of its cells is shown in Fig. 98. It is made of soapstone, in several sizes, one size being about 24 in. long, 12 in. wide, and 11 in. high. It has two terminal electrodes and a large number of intermediate (bipolar) electrodes. The electrodes are made of

¹ P. H. Prausnitz, *Z. Elektrochem.*, 19, 676 (1913).

graphite, and the intermediate electrodes have glass plates above and below them as shown in Fig. 98 to guide the flow of the brine. The brine, made up to a concentration of 60 g. sodium chloride per liter ($\frac{1}{2}$ lb. per gal.), enters the cell by way of one end compartment at the rate of 50 gal. per hr., preferably at a temperature 15 to 16° C. (60° F.), and leaves the cell at a little above 40° C. (104° F.), containing 6 to 7 g. of active chlorine per liter. An e.m.f. of 110 volts direct current is im-

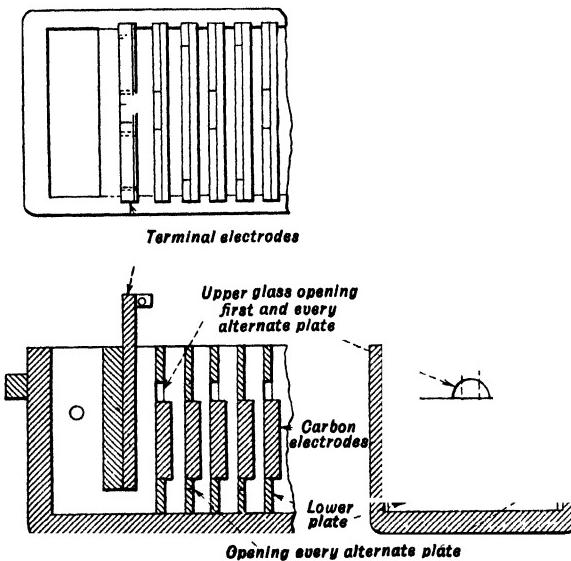


FIG. 98. Hypochlorite cell of the Electro Chemical Company.

pressed directly on the two terminal electrodes which delivers about 35 amp. through the cell. A cell of another size contains more electrodes and takes 220 volts. The energy yield is 3.5 kg. of hypochlorite per kw-day (3.1 kw-hr. per lb.).

The Kellner Cell. The Kellner cell using horizontal electrodes is considered one of the most efficient cells for the manufacture of electrolytic hypochlorite. It is shown diagrammatically in Fig. 99. The one shown is divided into six chambers arranged in terraces. The electrodes are bipolar and are made of a network of platinum-iridium wire. The chambers are separated by glass partitions. In order to illustrate the continuity of each electrode from one chamber to another the glass partitions are illustrated as though they fitted the grooves at the bottom loosely; in actual construction they fit firmly into the grooves so as to prevent flow of electrolyte beneath them. The brine, containing 15 per cent of sodium chloride, enters the upper cell through an opening in the

side wall. Part of the solution passes between the electrodes, which are about 0.2 in. apart, the anode below, the cathode above. Some

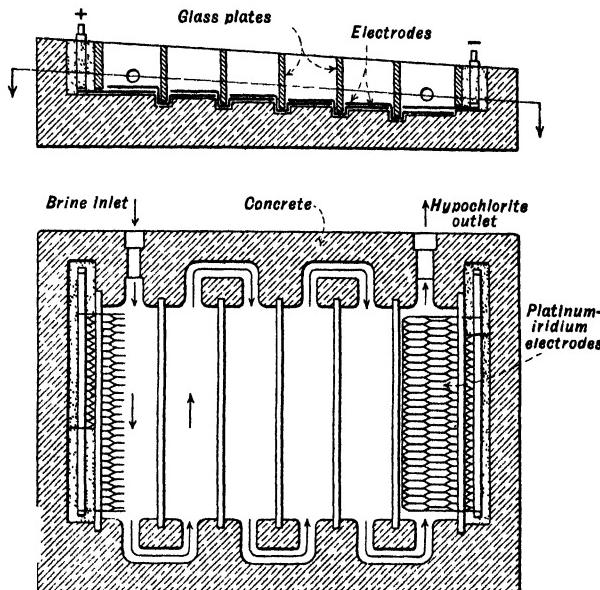


FIG. 99. Kellner horizontal hypochlorite cell.

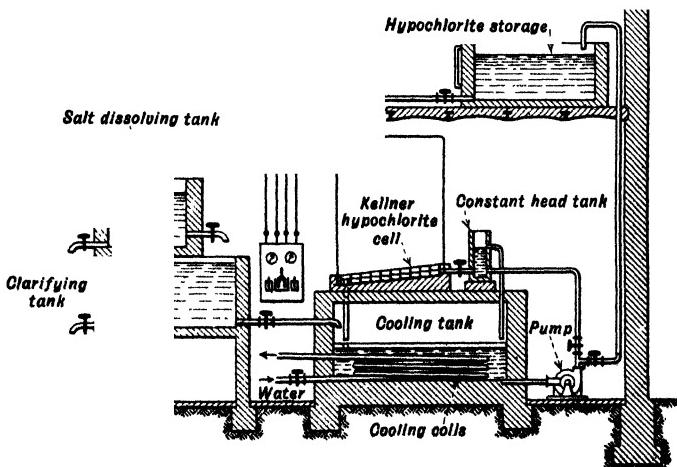


FIG. 100. Equipment for manufacturing sodium hypochlorite with a Kellner cell.

calcium chloride and Turkey red oil are added to increase the yield, as explained previously. The solution passes from one chamber to another and then out of the cell.

A liquor can be prepared containing 25 to 30 g. active chlorine per liter with an energy consumption of 6.2 kw-hr. per kg. (2.2 lb.) active chlorine. A solution with 90 g. per liter active chlorine can be produced at 9.3 kw-hr. per kg.

The solution is kept at a temperature of about 21° C. (70° F.). It is cooled after it leaves the cell and then recirculated through the cell; this is continued until the desired sodium hypochlorite concentration is obtained. Figure 100 shows the arrangement at one plant for preparing and clarifying the brine, cooling the brine and the hypochlorite, and the pump for circulating the solution.

The electrolytic production of sodium hypochlorite has reached much greater importance in Germany than in the United States. The Kellner horizontal cell and the Schuckert cell are among the leading ones used in Germany.²

Other Methods for Preparing Hypochlorites. Sodium hypochlorite is also made from calcium hypochlorite by double decomposition with sodium carbonate:



The calcium carbonate is allowed to settle, and the sodium hypochlorite liquor is drained off. Sodium hypochlorite cannot be made as cheaply per gram of available chlorine by this method as by direct electrolysis of sodium chloride, but it can be made in greater concentrations. Where only small amounts of sodium hypochlorite are needed occasionally this may be the most economical or most expedient method, especially if direct current is not readily available.

The method most common in the United States for making sodium hypochlorite is to treat a solution of sodium hydroxide with gaseous chlorine, which produces the hypochlorite as indicated in equation 6.

In either of these two methods, the manufacture of hypochlorite is generally, but not necessarily, dependent upon the electrochemical decomposition of sodium chloride in order to obtain chlorine in the first place and chlorine and sodium hydroxide in the second.

Uses of Sodium Hypochlorite. Both potassium and sodium hypochlorites can be made by the methods discussed above, but sodium hypochlorite is the only one of commercial importance. The hypochlorites are of value on account of their disinfecting, deodorizing, and bleaching qualities. As a disinfectant and deodorant sodium hypochlorite has special uses for dairies, creameries, public-water-supply and sewage-

² For a description of these and other cells the reader is referred to Victor Engelhardt, *Handbuch der technischen Elektrochemie*, II (2), Akademische Verlagsgesellschaft M.B.H., Leipzig, 1933.

disposal plants, and households. Those establishments requiring fairly large quantities of hypochlorites, like water-supply and sewage-disposal plants, the larger hospitals, and creameries, find it most economical to have one or more hypochlorite cells for making their own disinfectant. For smaller places and household uses, it can be bought ready prepared in bottles under the trade names Hyclorite, B-K (Bacili-Kil), Zonite, and others. As Dakin's solution (which contains some sodium chloride and boric acid, in addition to the hypochlorite), sodium hypochlorite was used during the first World War for irrigating wounds; it was the means of saving many lives and restoring to use limbs that would probably have been permanently stiffened without its aid.

As a bleaching agent, sodium hypochlorite finds use in the bleaching of cotton goods, linen, wool, jute, artificial silk, paper pulp, English walnuts, and oranges.

Sodium hypochlorite also has been used in the chlorination of some ores.

In many of the above-mentioned uses of sodium hypochlorite, bleaching powder, $\text{CaCl}(\text{OCl})$, and in others, liquid chlorine is also used, in some cases almost exclusively. This will be discussed more fully later.

The chemical action involved when sodium hypochlorite acts as a bleaching or disinfecting agent is discussed toward the end of the chapter along with that of bleaching powder and chlorine.

ALKALI CHLORATES

In discussing the reactions involved in preparing sodium hypochlorite we found three reactions that formed sodium chlorate, NaClO_3 :



This can also be written:



The other reactions are:



and



In the manufacture of hypochlorite it is necessary for efficient operation to suppress these reactions as much as possible, but in chlorate manufacture the object is to promote one or more reactions to their fullest extent.

The reaction represented by equation 11 can be accelerated very appreciably by adding hydrochloric acid and operating at elevated temperatures, say between 70° C. (158° F.) and the boiling temperature. If, therefore, a little free mineral acid be added to the sodium chloride solution, the concentration of hypochlorous acid (which is present in but small quantities in an alkaline solution during electrolysis) is very much increased. This increases the velocity of reaction 11 very much, so that chlorate is formed at the expense of hypochlorite. If cathodic reduction, equation 13, is avoided by the addition of chromate, and if the discharge of ClO^- , equation 8, can be avoided, chlorate could be formed with 100 per cent current efficiency. In practice, ClO^- discharge cannot be avoided entirely, so that current efficiencies of 85 to 95 per cent are obtained. The free hypochlorous acid is best obtained by the addition of hydrochloric acid to the liquors before electrolysis.

The reaction represented by equation 9 can be promoted by adding free alkali to the sodium chloride solution. The presence of alkali increases the concentration of ClO^- at the expense of HClO (which is a very weak acid, i.e., it is but slightly dissociated). Therefore in an alkaline solution there is a greater concentration of ClO^- than in a neutral solution, and the discharge of these ions with the consequent ClO_3^- formation, equation 11, is much accelerated. With increasing amounts of alkali in the electrolyte the formation of sodium chlorate, NaClO_3 , increases with a loss in the amount of hypochlorite, but the chlorate production cannot exceed 66 per cent current efficiency. With further addition of alkali, the oxygen evolution increases owing to discharge of OH^- , equation 7, and chlorate efficiency decreases.

In addition to the above reactions, if the temperature is above 40° C. (104° F.) a good share of any hypochlorite that is formed spontaneously forms chlorate and chloride:



Technical Cells for Chlorates

Practically all electrochemical production of chlorate is done with acid solutions. Platinum or graphite anodes and iron or copper cathodes are used.

One type of cell consists of an iron or cement container, rectangular in shape; a number of cells are connected in parallel electrically, but in series with respect to the flow of the liquor. The cells are arranged in terraces so that the electrolyte circulates by gravity. Each anode is placed between two cathodes. The anodes are of platinum-

iridium foil; the cathodes are of iron generally, but graphite has been used successfully. The electrolyte consists of a 25 to 30 per cent solution of sodium chloride or potassium chloride. Hydrochloric acid is added to bring the acid concentration of the electrolyte to about 0.05 *N*, and potassium dichromate is added, 10 g. per liter. The current density, 8 to 20 amp. per sq. dm. (74 to 185 amp. per sq. ft.), at the anodes is sufficient to heat the electrolyte, which enters the cells at room temperature, to 85 to 90° C. (185 to 194° F.).

If potassium chlorate is made, the liquor is recirculated through the cells until it is almost saturated. This occurs when the concentration reaches about 190 g. per liter at 85° C. (185° F.). The concentrated product is then cooled, and the chlorate, being the least soluble of the materials in solution, crystallizes out; a recrystallization gives a very pure salt. More potassium chloride is then added to the liquor and it is recirculated through the cells.

Sodium chlorate is more soluble than potassium chlorate (970 g. per liter as compared to 66 g. per liter water at 18° C.) and can therefore not readily be made by this method without modification. Fresh salt is continually added until the sodium chlorate concentration is about 700 g. per liter. A small amount of calcium hypochlorite is added to the electrolyte. On cooling, the greater part of the sodium chlorate crystallizes out.

Gibbs Process. In the Gibbs process, a large number of cells are connected so that the electric current flows through the cells in series, but the electrolyte flows through the cells in parallel. The electrodes are mounted on opposite sides of rectangular wooden frames. The anodes consist of platinum gauze mounted on lead backings. The cathodes are copper rods. The potassium chloride solution enters the bottom of each frame from a manifold, passes up between the electrodes, and goes out the top into another manifold. The evolution of hydrogen keeps the electrolyte well stirred.

The Barker Chlorate Cell.³ The Barker chlorate cell is used by the United Alkali Company. It is shown diagrammatically in Fig. 101. It consists of a rectangular iron tank, 5 to 8 ft. long, 2½ to 4 ft. high, and 8 to 16 in. wide. The bottom and lower part of the walls of the cell are lined with cement or concrete, and the top or cover is made of asbestos or asbestos concrete. Long cylindrical graphite anodes are suspended from the cover and hang in two rows, one along each side of the tank. In order to increase their life the anodes are impregnated

³J. T. Barker and the United Alkali Co., Ltd., Improvements in electrolytic cells . . . for use in the production of chlorates of the alkali metals, British Patent 173,028, Dec. 12, 1921.

with a synthetic resin or with paraffin. The cathode is placed between the two parallel rows of anodes and consists of iron cooling pipes and their supporting structure.

Groggins and his associates have given extensive reports on their experiments on the production of sodium chlorate.⁴

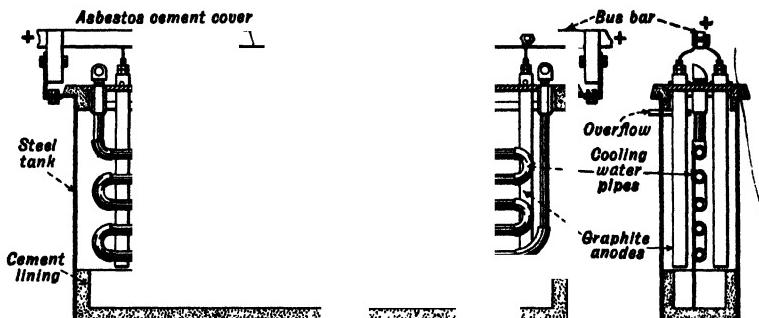
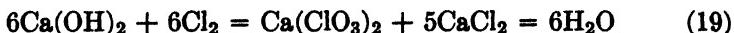


FIG. 101. Barker chlorate cell.

Other Methods for Preparing Chlorates. Potassium and sodium chlorates can also be made by non-electrochemical processes, except that the chlorine used is an electrochemical product. For either of the above chlorates, calcium hypochlorite is first made by treating milk-of-lime with an excess of chlorine at a temperature of about 65° C. (150° F.). The reaction is



In the manufacture of potassium chlorate, potassium chloride is added to the solution and the mixture is boiled down to a specific gravity of about 1.35, during which process chlorate is formed:

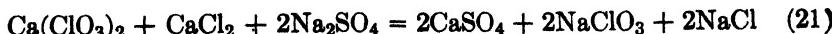


The solution is cooled, and the bulk of the potassium chlorate crystallizes; the salt is purified by recrystallization.

Sodium chlorate on account of its greater solubility is prepared somewhat differently. Calcium chlorate is prepared as above, and the resulting solution of $\text{Ca}(\text{ClO}_3)_2 + 5\text{CaCl}_2$ is boiled down to about 1.5 sp. gr. The greater part of the calcium chloride precipitates and is removed. The remaining solution is treated with sodium sulphate

⁴P. H. Groggins, A. L. Pitman, and F. H. Davis, *Chem. & Met. Eng.*, 47, 468 (1940).

which precipitates the calcium, both that of the chlorate and the remaining chloride, as calcium sulphate:



The resulting solution of sodium chlorate and chloride is boiled down, after which about 80 per cent of the sodium chloride is precipitated on cooling. More recently magnesium has been used in place of calcium in the preparation of chlorate.

CHLORINE-CAUSTIC CELLS

The electrolytic production of caustic and chlorine (NaOH or KOH , and Cl_2) involves the first step in the production of alkali hypochlorite (NaClO or KClO), namely, the electrolysis of an alkali chloride solution. The largest number of all caustic-chlorine cells in operation produces sodium hydroxide from a sodium chloride solution, and the fundamental reactions can be represented by:



Whereas in a hypochlorite cell the object is to produce intimate mixing of the sodium hydroxide and the chlorine to produce sodium hypochlorite, in the production of chlorine and caustic the object is to keep the two products apart so that they can be collected separately. In hypochlorite cells the electrodes are so placed that the electrode products can mix readily; in chlorine-caustic cells special means are used to check diffusion of the electrode products toward each other. The various means employed to reduce diffusion will be discussed in the next section.

Classification of Chlorine-Caustic Cells

Diaphragm Cells. In diaphragm cells there is placed between the anode and cathode a diaphragm of a material that will allow ions to pass through by electrical migration yet will reduce the diffusion of the products liberated at the electrodes. The moment the circuit is closed, all the Cl^- and OH^- ions move toward the anode and all the Na^+ and H^+ ions move toward the cathode.

If we consider the electrolyte stationary, the moment the circuit is closed, dissolved chlorine will move from the anode toward the cathode by diffusion. At the same time OH^- ions will move from the cathode toward the anode by diffusion and by migration. At first, the alkali and the chlorine (and acid if any is present) each diminishes in concentra-

tion to a zero point at some distance from their respective electrodes. After a time these advancing fronts meet, and interaction takes place, producing water and hypochlorite:



If the solution is not disturbed there will be three distinct zones, each with a fairly sharp boundary: a chlorine zone, a narrow neutral zone containing the ClO^- ions, and an alkaline zone. But the amount of alkali (OH^- ions) moving toward the anode is more than enough to react with the advancing dissolved chlorine, so the neutral zone steadily moves toward the anode as electrolysis proceeds, but with decreasing velocity. Finally the alkali zone will reach the anode, and there will be a free interaction between the alkali and the liberated chlorine, and the current efficiency from the point of view of chlorine and caustic production will drop very much. To avoid this, the cells are made continuous in operation; the brine solution enters near the anode and moves toward the cathode and out of the cell. The rate of flow may be so adjusted that the neutral zone not only is stationary, but also can be held at any desired location between the anode and cathode. The rate of flow, however, for a definite brine concentration and current density will determine the concentration of sodium hydroxide in the effluent.

In order to reduce diffusion, a diaphragm may be placed between the anode and cathode; from the point of view of current efficiency and alkali concentration in the effluent, the rate of brine flow should be such that the neutral zone is located in the diaphragm. If the rate of flow is too great, the alkali concentration in the effluent will be low; if the rate of flow is too low, the neutral zone will move toward the anode side of the diaphragm, and if the diaphragm is vertical the alkali will be acted on by the chlorine, which will cause more alkali to diffuse anodeward. Furthermore, if the brine flow is either too great or too low, the current efficiency will drop.

Diaphragms are generally made of asbestos, commonly of asbestos paper, ranging in thickness from 0.01 to 0.05 in., and are placed near or in contact with the cathode; in the latter case the cathode also serves as a support for the diaphragm. The cathode may be made of iron gauze or perforated sheet iron; the anode, of carbon or graphite or of magnetite.

Cells may be constructed with vertical or horizontal diaphragms. Cells with vertical diaphragms are shown diagrammatically in Figs. 102 and 103; with horizontal diaphragm, in Fig. 104. In cells with horizontal diaphragms the cathode is placed horizontally in the cell with the anode

above it. Vertical diaphragms seem to be preferred; they allow greater accessibility and greater compactness, and sediment, instead of settling on the diaphragm, falls to the bottom of the cell. In horizontal diaphragms, however, the diffusion is more uniform, for the hydrostatic pressure is distributed evenly over the whole diaphragm.

Vertical diaphragms may be of the submerged or unsubmerged type. In the submerged type, Fig. 102, the overflow pipe from the cathode chamber is so arranged that the chamber is filled with the caustic solution. In the unsubmerged diaphragm type, the cathode liquor is drained

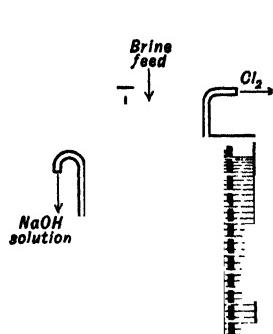


FIG. 102. Chlorine-caustic cell, submerged vertical diaphragm.

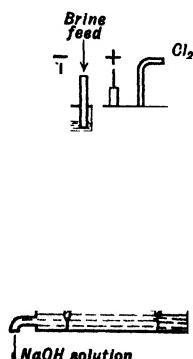


FIG. 103. Chlorine-caustic cell, unsubmerged vertical diaphragm.

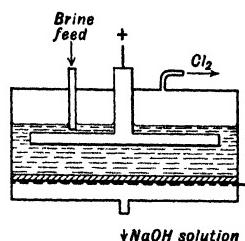


FIG. 104. Chlorine-caustic cell, horizontal diaphragm.

from the chamber as fast as it is formed. This type seems to be preferred by users. The advantage of the unsubmerged over the submerged type is that the OH⁻ ions are removed more rapidly from the diaphragm and therefore do not have as good an opportunity to migrate to the anode. The rate of percolation is faster, and therefore higher current densities are necessary, but this allows greater capacity for a given size cell. Also, steam can be admitted to the cathode chamber, to help remove the sodium hydroxide and also to raise the temperature, which lowers the resistance of the electrolyte and of the diaphragm. However, steam dilutes the caustic obtained, and preferred practice seems to be to heat the incoming brine. The disadvantage of the unsubmerged diaphragm is that the difference in hydrostatic pressure between the top and bottom of the diaphragm causes different rates of percolation, so that, if the rate is adjusted to one part of the diaphragm for most efficient operation, it is either too slow or too fast at other parts. This uneven percolation can be avoided by gradually increasing the thickness or the density of the diaphragm from top to bottom. However, in uniform diaphragms

the rate of flow soon is adjusted automatically with use, for precipitated hydroxides and particles of graphite or carbon from the anode fill the pores of the diaphragm wherever the flow of the brine is most rapid.

Diaphragms permit the construction of compact cells, for the electrodes can be placed fairly close together; but the diaphragms, on account of their resistance, require a higher voltage and higher hydrostatic pressure on the brine feed. The diaphragms may not always be uniform in thickness or in porosity, so that, when the hydrostatic pressure is properly adjusted for one part of the diaphragm, the rate of brine flow may be too high or too low at other parts. Diaphragms also will eventually clog and must be replaced periodically.

Bell-Jar Cells. In the bell-jar process, the anode is surrounded by a bell jar as illustrated in Fig. 105. The cathode is outside the jar, and the

chlorine liberated at the anode escapes through the top of the jar. As in the diaphragm cells, three layers or zones are formed in the electrolyte. The upper layer is saturated with chlorine, a neutral zone containing ClO^- ions is below this, and then an alkaline zone. The brine enters the anode compartment, and its downward flow prevents the OH^- ions from reaching the anode. The relatively great distance between the electrodes as compared with most other types of cells increases the resistance of the cell and consequently the required operating voltage.

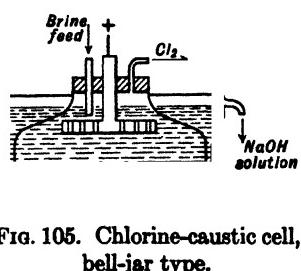


FIG. 105. Chlorine-caustic cell, bell-jar type.

between the electrodes as compared with most other types of cells increases the resistance of the cell and consequently the required operating voltage.

Mercury Cells. Another method for separating the anode and cathode products is to deposit the sodium or potassium in a mercury cathode, the alkali metal forming an alloy or amalgam with the mercury. The dilute sodium amalgam may be removed and treated with steam, as is the lead-sodium alloy in the Acker cell, or the mercury may be a bipolar electrode, as in the Castner cell, shown diagrammatically in Fig. 106. Here extends into another compartment of the cell, where the sodium plates out of the mercury and then immediately reacts with the water of the electrolyte to form sodium hydroxide and hydrogen.

In the discussion under the general theory at the beginning of this chapter, mention was made of the fact that theoretically, when sodium chloride solution is electrolyzed between insoluble electrodes, not sodium but hydrogen is discharged directly. This is based on the fact that from a neutral sodium chloride solution, normal with respect to Na^+ ions, a potential of -2.71 volts is required to discharge the Na^+ ions, but only 0.4 volt to discharge H^+ ions. If, however, the ionic ratio $\text{Na}^+ : \text{H}^+$

is very high, Na^+ ions will be discharged preferentially; or if the electrolytic solution pressure of sodium is lowered by its being discharged as an alloy with the cathode, the Na^+ will also be preferentially discharged. In a mercury-cathode cell, whether the cathode be independent or part of a bipolar electrode, sodium is discharged directly. But in the use of a mercury cathode, the current density must not be too low, for the increased overvoltage of hydrogen on mercury at higher current densities is a factor in preventing the deposition of hydrogen. In addition, the sodium must be continually removed from the amalgam in order to keep the solution pressure of the sodium sufficiently low, or hydrogen and not sodium will be deposited.

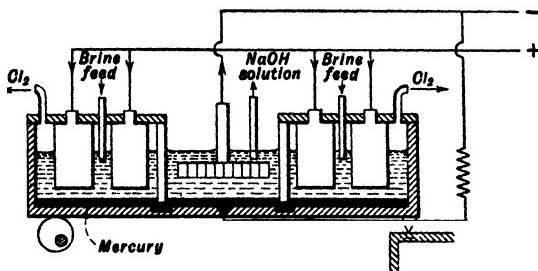


FIG. 106. Chlorine-caustic cell, intermediate mercury electrode.

The current efficiency of mercury cells is not 100 per cent, but more nearly 95 per cent. The factors decreasing the efficiency may be summed up as follows: Hydrogen ions may be discharged if the current density is low or if the amalgam becomes too concentrated. The sodium in the amalgam may combine with the water of the electrolyte by direct chemical interaction. Although this interaction is slow at room temperatures, it becomes important at 60°C . (140°F) so that in practice the cell temperature should be below this point. In addition, dissolved chlorine diffusing to the cathode may give up electrons, so that all the electrons entering the cell do not discharge sodium. In other words, instead of the desired reaction



the following may also take place:



Calculations

Current Efficiency. The current efficiency of chlorine-caustic cells is determined by dividing the actual amount of sodium hydroxide or

chlorine produced per unit of time by the theoretical maximum that could be produced according to Faraday's laws. A convenient unit to use is pounds per 1,000 amp-hr., which can be obtained from Table V, page 24. For sodium hydroxide the theoretical maximum is 3.29074; for chlorine it is 2.91626 lb. per 1,000 amp-hr.

C.E. for caustic production

$$= \frac{(\text{Lb. NaOH produced per 1,000 amp-hr.}) \times 100}{3.29074} \text{ per cent}$$

C.E. for chlorine production

$$= \frac{(\text{Lb. Cl}_2 \text{ produced per 1,000 amp-hr.}) \times 100}{2.91626} \text{ per cent}$$

Energy Efficiency. The energy or power efficiency is equal to the product of the decomposition potential of sodium chloride and the current efficiency, divided by the operating voltage of the cell. The decomposition potential of sodium chloride can be taken as 2.3 volts, so that

$$\text{E.E.} = \frac{2.3 \times \text{C.E.} \times 100}{\text{Operating voltage}} \text{ per cent}$$

Production per Kilowatt-Hour. For sodium hydroxide and chlorine, the actual production per kilowatt-hour is equal to the product of the theoretical production per ampere-hour, the current efficiency, and 1,000 divided by the operating voltage of the cell, thus:

$$\text{Lb. caustic per kw-hr.} = \frac{(\text{Lb. NaOH per amp-hr., theor.}) \times 1,000 \times \text{C.E.}}{\text{Operating voltage}}$$

$$3.29074 \times \text{C.E.}$$

$$\text{Operating voltage}$$

$$\text{Lb. chlorine per kw-hr.} = \frac{2.91626 \times \text{C.E.}}{\text{Operating voltage}}$$

Preparation of the Brine

The brine used in chlorine-caustic cells is usually a saturated solution of sodium chloride. This may be a solution from salt wells, but more commonly it is obtained by dissolving rock salt. The rock salt is placed in a dissolving tower in which water is admitted from the bottom and leaves at the top. The rate of flow is so adjusted that the water becomes saturated by the time it leaves the tower.

Although the salt used is fairly pure as a commercial article, it is necessary to remove the small amounts of calcium salts usually present. Sometimes magnesium salts may also be present in sufficient amount to require removal. If these compounds are not removed, calcium and magnesium hydroxides will be formed in the diaphragms of the cells which will clog them prematurely. The saturated brine is therefore treated with a sodium carbonate solution, usually prepared from soda ash. The contents of the tank are agitated by means of paddles or compressed air. The calcium and magnesium carbonates formed are allowed to settle in a settling tank, after which the clear brine is siphoned into a neutralizing tank. In this tank, hydrochloric acid is added to neutralize the excess sodium carbonate. At the Edgewood Arsenal plant constructed during the first World War, arrangements were made to prepare the hydrochloric acid synthetically at the plant from the chlorine and hydrogen from the electrolysis cells.

Generally rock salt does not contain enough soluble sulphates to warrant their removal. If any considerable quantity is present its electrolysis results in excessive oxidation of the anodes and an abnormal increase in the percentage of carbon dioxide in

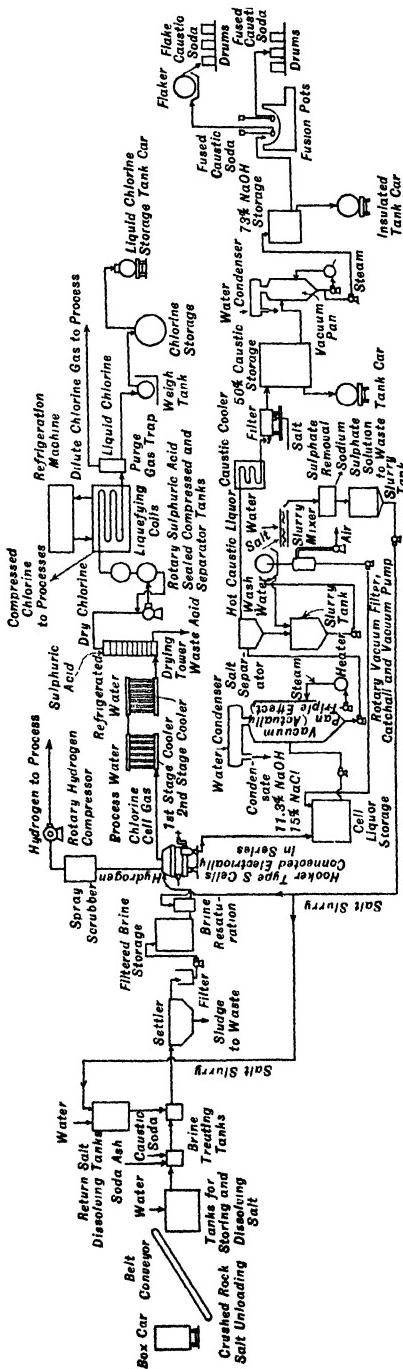


FIG. 107. Electrolytic chlorine and caustic soda. *(Courtesy Chemical and Metallurgical Engineering.)*

the chlorine. Sulphates are removed by precipitation with barium chloride.

Diaphragm Cells

Allen-Moore Cell. The new Allen-Moore type KML cell is manufactured by the Electron Chemical Company; it is illustrated in Fig. 108

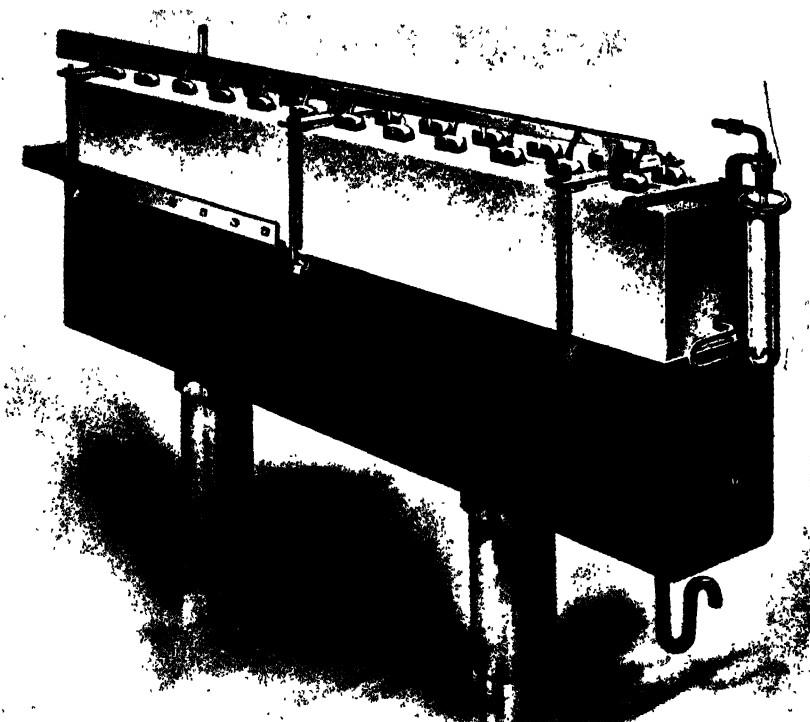


FIG. 108. Allen-Moore type KML chlorine-caustic cell. (*Courtesy Electron Chemical Company.*)

and in cross-section in Fig. 109. It is of the unsubmerged-cathode type, the caustic liquor flowing down the cathode and out the bottom. The anodes are preferably of graphite, but retort carbon or fused iron oxide also give good service. The cathode is made of perforated iron lined with asbestos cloth on the anode side. The brine is fed to the anode compartment and is maintained at a constant level automatically.

The cell is 8 ft. 6 in. long, 1 ft. $2\frac{1}{2}$ in. wide, and 3 ft. high, and weighs about 1,330 lb.

The cells operate at 1,500 amp. per cell and about 3.6 volts. The current efficiency is guaranteed to be 92 per cent, but 95 to 97 per cent is

said to be common. The energy efficiency based on a 95 per cent current efficiency is 61 per cent. Each cell will produce 0.87 lb. sodium hydroxide and 0.77 lb. chlorine per kw-hr. The cathode liquor contains about 130 g. sodium hydroxide and 140 g. sodium chloride per liter.

The Allen-Moore cell is widely used, being installed in about a dozen plants in the United States and in a large number of foreign plants.

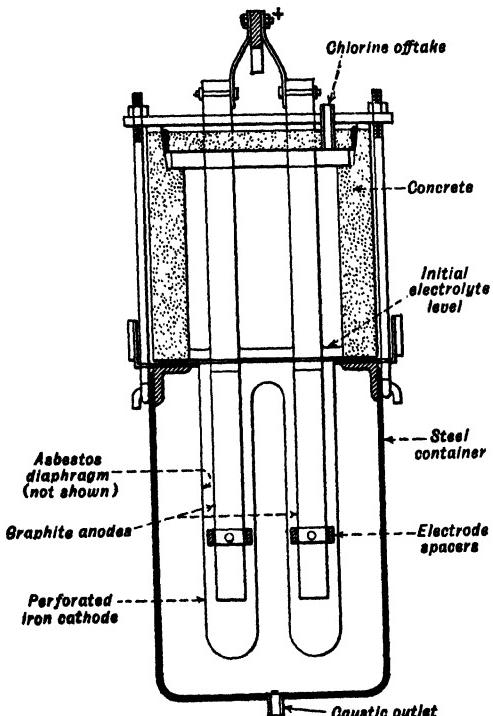


FIG. 109. Allen-Moore type KML chlorine-caustic cell in cross-section.

There are installed a total of 4,500 cells, having a daily capacity of 240 tons sodium hydroxide and 213 tons of chlorine.

The Nelson Cell. The Nelson cell⁵ shown in Figs. 110 and 111 is rectangular in shape. It contains 14 graphite anodes 4 by 4 by 17 in. placed vertically in a plane. A U-shaped cathode of perforated sheet steel is placed so that the anode assembly fits centrally in the trough formed by the cathode. The inner side of the cathode is lined with an asbestos diaphragm; the ends of the diaphragm are closed with blocks of portland cement; this forms the anode compartment. An outer con-

⁵ C. F. Carrier, *Trans. Am. Electrochem. Soc.*, 35, 239 (1919); and *Chem. & Met. Eng.*, 21, 183 (1919); S. M. Green, *ibid.*, 21, 17 (1919).

THE ELECTROLYSIS OF ALKALI HALIDES

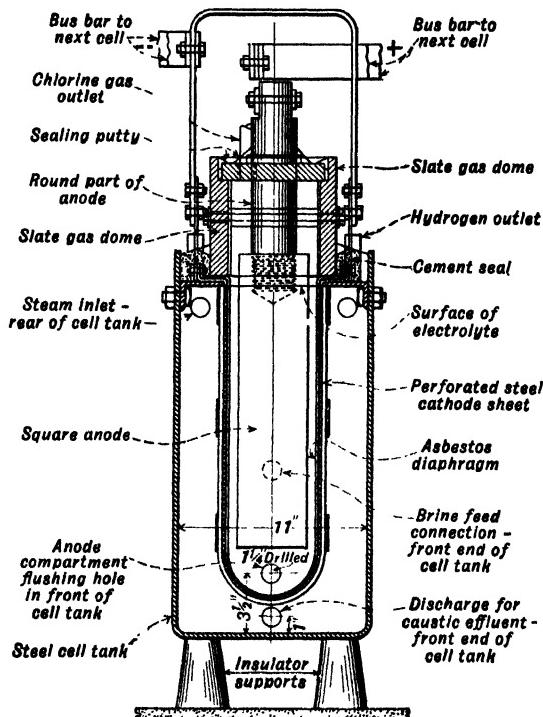


FIG. 110. Nelson chlorine-caustic cell in cross-section.

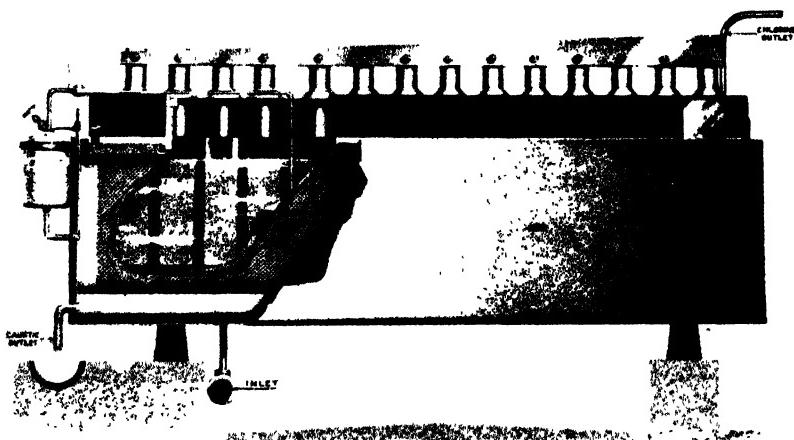


FIG. 111. Nelson cell showing interior arrangement. (Courtesy H. R. Nelson.)

taining tank made of steel surrounds the cathode and forms the cathode space. The cell is closed at the top by an inverted box of slate slabs. Graphite connectors or lead-ins pass through the top of the slate box; the lower ends of these graphite rods are threaded, and the anodes are screwed to them. The brine, purified, enters the anode compartment; its flow is controlled by a float which operates a dull knife edge against a section of rubber tubing; a slight rise of the brine level stops the flow of brine entirely, and a small drop in the level admits more brine. The Nelson cell is of the unsubmerged-cathode type; the caustic drops to the bottom of the cathode chamber and out through a drain. Steam is blown through the cathode chamber; it helps to remove the caustic from the cathode, and its heating effect decreases the resistance of the cell.

The anodes last one or two years, depending on whether or not they are impregnated to prevent brine from creeping up to the copper connecting bar. The diaphragms last 6 to 8 months and the cathode plates 2 to 5 years. With these replacements, cells have been in operation for 25 years.

The cells are built to operate at 1,000 amp. and require an average e.m.f. of 3.7 volts. The current efficiency is about 94 per cent, and on this basis the energy efficiency is 58.5 per cent. This corresponds to about 0.835 lb. sodium hydroxide and 0.74 lb. chlorine per kw-hr. The cathode alkali contains 100 g. sodium hydroxide and 150 g. sodium chloride per liter.

Vorce Cell. The Vorce cell, in wide commercial use, is illustrated in Fig. 112, which is almost self-explanatory. Its over-all dimensions are 26 in. in diameter and 42 in. high. The cell is constructed with three cement rings or sections. The lower one serves as the bottom of the inside of the cell, which with an upper annular ring supports the cathode. Resting on the upper ring is a cover, somewhat bell-shaped; it supports the graphite anodes and also collects the chlorine. These concrete parts are made of a mixture of portland cement and ground asbestos. The 24 anodes are made of Acheson graphite and are about 2 in. square in cross-section. The upper threaded end of each anode projects through the bell-shaped cover and is held in place by a hard-rubber or lead nut. The upper end of each electrode is bolted to a copper ring which connects all the anodes in parallel electrically. The weight of the anode assembly is about 200 lb., and the anodes last about 84 weeks. The diaphragm is made of long-fiber asbestos and is in direct contact on the inside of the cylindrical cathode, which is of perforated sheet steel.

At the Westvaco Chlorine Products, Inc., South Charleston, West Virginia, the brine at a constant head of 14 in. is fed to cells through an

automatic regulator which keeps the liquor in the tank at such a height that the lower part of the upper concrete cathode ring is immersed; this prevents hydrogen from mixing with the chlorine. The caustic liquor flows down the outside of the cylindrical electrode and out through a bottom outlet into a collecting main and then to the evaporating house. The chlorine is withdrawn from the top of the cell through glass connections to stoneware collection mains. The gas in the mains is generally under a slight vacuum, but the cells can operate at a pressure of 2 to 4 in.

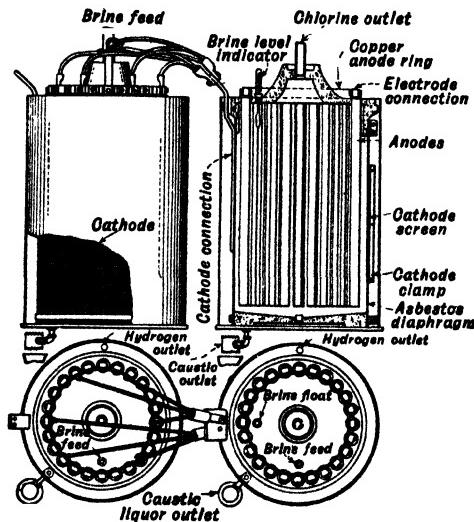


FIG. 112. Vorce single-cathode chlorine-caustic cell.

above or below atmospheric. The chlorine passes through coolers and then two drying towers where it passes against 66° Bé. sulphuric acid. The hydrogen is collected through an opening in the upper cathode ring. Each series of 70 cells is operated at 250 volts with 1,000 amp. through each cell.

Table XXVI⁶ shows the results of monthly test runs made on Vorce cells at Westvaco Chlorine Products, Inc.

The Vorce cell was developed by Dr. L. D. Vorce in 1917. In 1927 Westvaco Chlorine Products, Inc., installed 2,240 Vorce cells; the total at the plant is now over 3,600. Additional cells have been installed in Russia, China, India, and South America.

The Vorce cell is also made with a double cathode. A smaller cylindrical cathode and diaphragm are placed concentrically within the outer cathode, giving 60 per cent more cathode surface, increasing the produc-

⁶ S. D. Kirkpatrick, *Chem. & Met. Eng.*, 35, 158 (1928).

TABLE XXVI
DATA ON VORCE SINGLE-CATHODE CELLS

Specific gravity of cathode liquor	1.211
Percentage of NaOH	8.607
Percentage of NaCl	15.79
Percentage of Na ₂ CO ₃	0.115
Percentage of NaClO	Trace
Percentage of NaClO ₃	0.068
Percentage of Cl ₂ in gas	98.3
Percentage of CO ₂	0.7
Gallons of liquor per cell per hour	3.417
Pounds of caustic per cell per day	71.42
Pounds of chlorine per cell per day	63.15
Pounds of caustic per kw-hr.	0.859
Pounds of chlorine per kw-hr.	0.793
Average amperes per cell	948.1
Average volts per cell	3.5
Temperature of brine, °F.	147.
Current efficiency, per cent	94.84
Energy efficiency, per cent	62.11

tion 60 per cent, and reducing the voltage. A double-cathode cell is shown in Fig. 113.

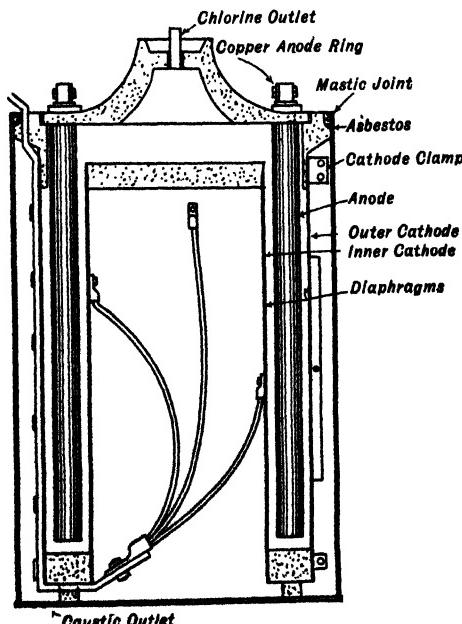


FIG. 113. Vorce double-cathode cells

The Gibbs Cell. The Gibbs cell⁷ was one of the earliest cylindrical-type vertical-anode cell made. The construction has been modified in late years; Fig. 114 shows a view of the cell as probably constructed now.

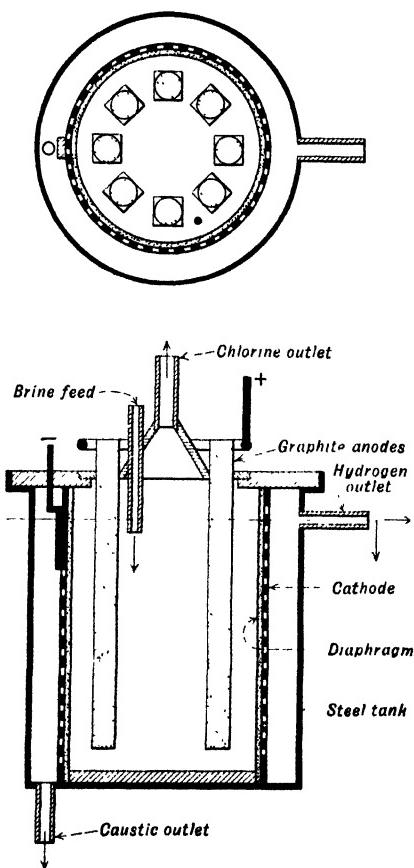


FIG. 114. Gibbs chlorine-caustic cell.

In the earlier design the sheet-iron cathode was punched with a large number of holes, the rough edges of the holes projecting inward, thus helping to support the diaphragm, which was not made of asbestos paper but was built up of asbestos fibers. The punched edges projecting into the cathode were also said to decrease the electrical resistance of the cell and to promote better operation. The diaphragm increased in thickness toward the bottom to produce uniform percolation of the electrolyte with increasing hydrostatic pressure toward the bottom.

In the Gibbs cell, according to the original patent, the cathode was submerged in the electrolyte, that is, the cathode compartment was filled with alkali. In the cell as now used the cathode is not submerged; i.e., the brine percolates through the anode, is partially converted to caustic, and flows down the cathode and out the cell. An asbestos paper diaphragm is used in the new cells.

The first installation of Gibbs cells was in 1904, at the Wyandotte, Michigan, plant of the Pennsylvania Salt Manufacturing Company, and since then these cells have been installed in the Menominee, Michigan, and Tacoma, Washington, plants of the same company. The cell is also used by the Canadian Salt Company, Windsor, Ontario, and by the United Alkali Company of Widnes, England. The combined capacity of the 10,600 Gibbs cells by the above-named companies is 214 tons of chlorine per day.

⁷ A. E. Gibbs, Electrolytic cell, U. S. Patent 874,064, Dec. 17, 1907.

The Gibbs cell operates at 800 amp. per cell at 3.44 volts. The current efficiency averages 93.5 per cent, which corresponds to an energy efficiency of 62.5 per cent. On this basis the cells produce 0.795 lb. sodium hydroxide and 0.705 lb. chlorine per kw-hr. The cathode effluent contains 120 g. sodium hydroxide and 155 g. sodium chloride per liter.

Wheeler Cell. The Wheeler cell⁸ is also a cylindrical vertical-diaphragm-type cell. An assembled cell is shown in Fig. 115. The

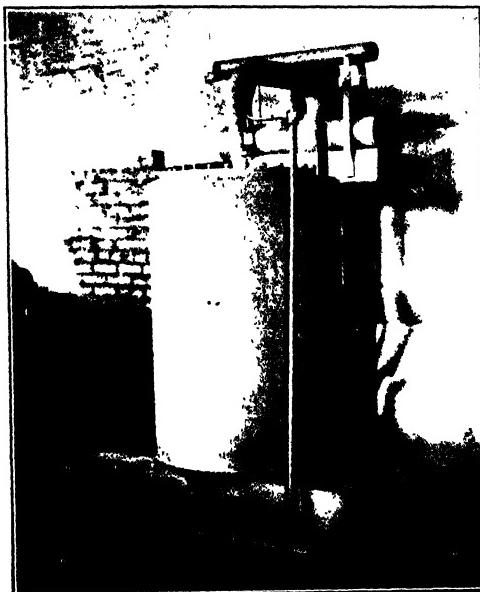


FIG. 115. Wheeler Type M chlorine-caustic cell.

base and cover are made of a concrete consisting of quartz sand, asbestos fiber, and cement. The cell contains a hollow column rising from the base of the cell, and at the top of the column is supported the cover which holds the anodes. The weight of the cover and anodes is therefore carried by the central column. The brine is fed directly into the anode compartment through the top of the cell. A float device controls the level of the electrolyte in the cell and also breaks any current leakage back through the brine feed so that iron brine lines can be used.

The graphite anodes are 28 in number, 32 in. long and 2 in. square. The cell itself is about 28½ in. in diameter and 42 in. high. The diaphragm life is about 160 days, and the anode life 450 to 500 days.

⁸ F. G. Wheeler, *Chem. & Met. Eng.*, 21, 436 (1919). This article describes the earlier type of Wheeler cell.

The cathode is made of wire cloth with elongated meshes, the longer side of the meshes being horizontal. A special composition wire is used to prevent or reduce hydrogen-caustic embrittlement.

A special feature of the cell is its thin diaphragm, which is said to have the following advantages: A thin diaphragm reduces the migration of OH^- ions toward the anode; a thick diaphragm retains the sodium hydroxide solution between the electrodes and so places the OH^- ions in



FIG. 116. Cathode assembly, Wheeler chlorine-caustic cell.

the electrical field. It is desired to have a structure that will permit the sodium hydroxide to be removed from this field as quickly as possible, and a thin diaphragm aids in this. A thin diaphragm does not plug up with impurities as quickly as a thick one and so keeps uniform and open over a longer period. When a diaphragm becomes sluggish the flow of the brine may be reduced so much that the migration of the OH^- ions toward the anode is greater than the rate of flow of the brine outward. This causes a drop in the efficiency of the cell, an impure caustic effluent, formation of carbon dioxide in the chlorine, and corrosion of the graphite anodes.

Figure 116 shows a cathode assembly. The current density, based on the area of the diaphragm, is 5 amp. per sq. dm. (47 amp. per sq. ft.). For average figures the current per cell can be taken as 1,000 amp. at 3.6

volts. The current efficiency is guaranteed at 95 per cent but may be as high as 98 per cent. The energy efficiency is about 62 per cent, which corresponds to 0.87 lb. sodium hydroxide and 0.77 lb. chlorine per kw-hr. The cathode alkali averages 110 g. sodium hydroxide and 155 g. sodium chloride per liter. The hydrogen and chlorine are each 98 per cent pure.

The Hooker Cell. The Hooker cell (designated as the Type S cell) has been described by its chief designer and his associates.⁹

The cell, shown in section in Fig. 117, consists of three sections, bottom, middle, and top, placed one above the other. The concrete top

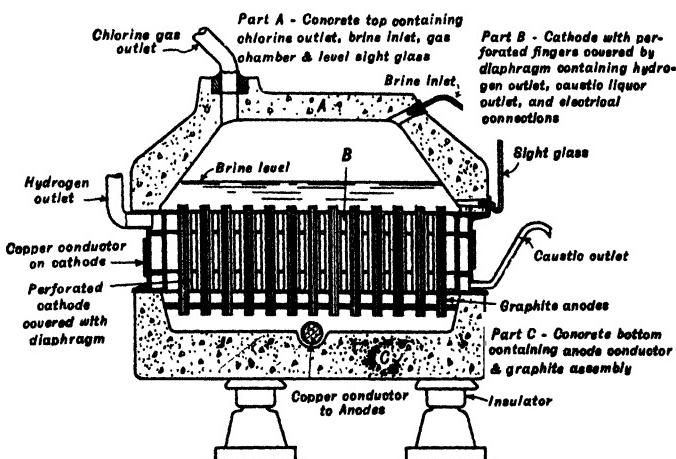


FIG. 117. Hooker cell in section. (Courtesy Hooker Electrochemical Company.)

and bottom sections serve merely for support and as containers for brine and chlorine. The active middle section consists of rows of flat anodes alternating with asbestos-covered wire screen cathode chambers. Within this section, which is 4 by 5 ft. and 1 ft. high, are approximately 130 sq. ft. of active cathode surface and 110 sq. ft. of active anode surface, permitting satisfactory operation at 7,000 amp.

For coating the wire cathode chambers, a suspension of asbestos fiber is prepared using a definite proportion of fibers of various lengths so that a strong diaphragm is produced with the correct degree of porosity. The wire cathode chambers are placed in this suspension, suction is applied to the inside of the chambers, and the asbestos fibers are deposited on the outside, the action being somewhat like that of the Sweetland filter, the precipitate being the deposited diaphragm.

⁹ K. E. Stuart, T. L. B. Lyster, and R. L. Murray, *Chem. & Met. Eng.*, **45**, 354 (1938); R. L. Murray, *Trans. Am. Inst. Chem. Engrs.*, **36**, 445 (1940).

The graphite anodes are flat parallel plates as shown in Fig. 118, connected at their lower ends to a lead conductor. The saturated brine is admitted through the top of the cell through a tube so designed that it breaks the brine stream into a spray to avoid current leakage and to cause circulation and mixing of the brine. Chlorine evolved at the anode escapes through the brine into the dome at the top of the cell. At the cathode, hydrogen is evolved as the brine percolates through the dia-

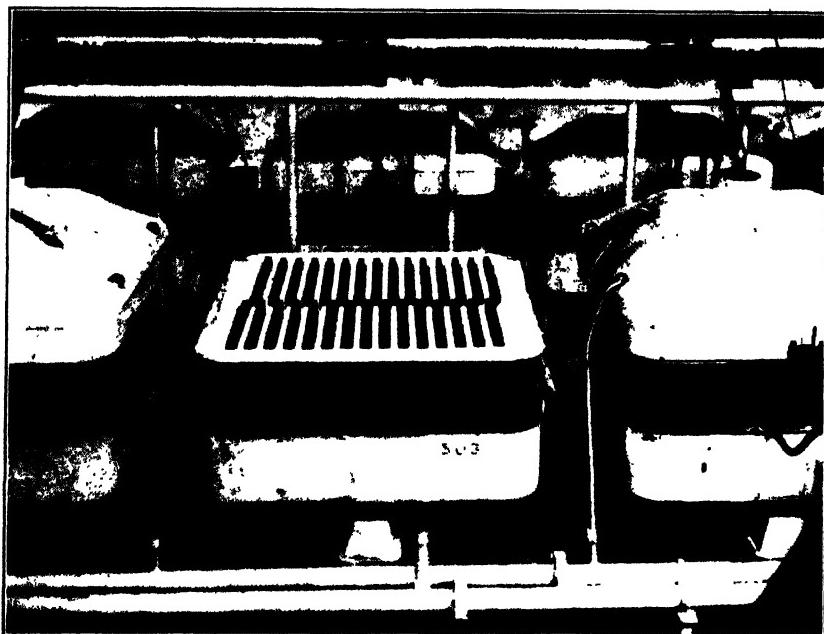


FIG. 118. A Hooker cell, cover removed. (*Courtesy Hooker Electrochemical Company.*)

phragm; the alkali brine collects in the cathode compartment and is conducted out of the cell through the gooseneck.

The liquid level in the cathode compartment is maintained near the top of the cathode, thus making it a submerged-diaphragm cell, which is contrary in practice to most of the other diaphragm cells in use.

As the pores of the diaphragm become clogged with precipitate the liquid level in the anode compartment is raised, thereby increasing the head. The amperage and brine feed are held constant for a given rate of production, the voltage being variable. The voltage varies from 3.28 to 3.25; the current density from 38 to 54 amp. per sq. ft. at the cathode. The current efficiency is 94 to 95.5 per cent; the energy efficiency, 67 to 70 per cent. The cell will produce 0.91 to 0.94 lb. caustic and 0.81 to 0.84 lb. chlorine per kw-hr.

An installation of Hooker type S cells is shown in Fig. 119.

The Marsh Cell. The Marsh cell¹⁰ (designated as the Hooker Type E cell) is of a somewhat different design from other cells so far discussed. The anodes, made of graphite rods $1\frac{3}{4}$ in. in diameter and 24 in. long are placed horizontally one above another, with spaces between about $1\frac{3}{4}$ in. wide. They are attached for support to a vertical graphite bar, which also acts as an electrical conductor. Two such anode assemblies, containing 4, 6, or 10 electrodes each, are supported with their "backs"



FIG. 119. An installation of Hooker cells. (*Courtesy Hooker Electrochemical Company.*)

toward each other. The cathode consists of perforated sheet steel, corrugated horizontally to conform to the surface of the anodes. Asbestos paper diaphragms are placed on the cathode so as to conform to the corrugations. The cathode is then clamped against the top of the cell and the concrete ends of the cell, the diaphragms acting as gaskets. The cathode and the ends and the top thus form the electrolytic compartment. This unit is placed in a boxlike structure, or a series of cells can be placed in a single structure, forming a large unit.

The cells are made up in units ranging in capacities from 50 to 5,000 amp. The 50- to 100-amp. units average 3 volts with a current efficiency of 94 per cent. On this basis the energy efficiency is 72 per cent. The low voltage is due to the large electrode surface made possible by the corrugated cathodes. The above voltage and current efficiency correspond to 1.03 lb. sodium hydroxide and 0.96 lb. chlorine per kw-hr. The cathode alkali contains about 120 g. sodium hydroxide and 150 g. sodium chloride per liter. Under normal conditions the cells operate 6 months or

¹⁰ C. W. Marsh, *Trans. Am. Electrochem. Soc.*, 39, 507 (1921).

longer without requiring replacement of diaphragms; the anodes last 2 years.

The Marsh cell, used by the Hooker Electrochemical Company, has been replaced almost entirely by their type S cell.

The Townsend Cell. The Townsend cell¹¹ (designated as the Hooker type F cell), also a product of the Hooker Electrochemical Company, is shown in Figs. 119 and 120. Although it is of the unsubmerged-cathode type, a distinctive feature is that the cathode compartment, instead of being empty as in other cells of this type, contains kerosene or other light oil. The cathodes consist of perforated iron plates with diaphragms placed directly against them on the anode side. The anodes are graphite and are located within 1 cm. of the cathode. Another feature of this cell is that the brine, instead of all passing through the diaphragm and being converted to sodium hydroxide at whatever percentage the cell is capable of, is pumped into the anode compartment and out again to be resaturated. This gives a high brine content in the anode chamber. The kerosene in the cathode chamber serves mainly to give a back-pressure to the brine on the other side of the diaphragm. This permits the use of a thin diaphragm, which in turn permits more uniform percolation and a lower voltage for the cell. The sodium hydroxide produced forms oily-looking drops which separate from the cathode and fall to the bottom. The effluent is drawn out of the bottom of the cathode compartment through "goosenecks."

FIG. 120. Hooker or Townsend chlorine-caustic cell.

pressure to the brine on the other side of the diaphragm. This permits the use of a thin diaphragm, which in turn permits more uniform percolation and a lower voltage for the cell. The kerosene level can be adjusted to control the rate of percolation. The sodium hydroxide produced forms oily-looking drops which separate from the cathode and fall to the bottom. The effluent is drawn out of the bottom of the cathode compartment through "goosenecks."

The Townsend cell, like the Marsh cell, has been replaced almost completely by the type S cell.

Giordani-Pomilio Cell. This cell, shown in section in Fig. 121, is rectangular in shape and can be operated either as a submerged or partially submerged diaphragm cell. The outlet of the gooseneck can be raised and lowered to obtain different heights of liquid level in the chamber back of the cathode; a variation of more than 3 ft. in the static head is possible. The pores of the diaphragms become filled with sediment in all types of cells. As the pores become stopped the liquid level in the outer chambers can be lowered to increase the head, and thus a

¹¹ A. H. Hooker, *Trans. Am. Inst. Chem. Engrs.*, 18, 55 (1920).

constant volumetric flow of liquid can be attained throughout the life of the diaphragm.

A cement frame forms the top, ends, and bottom of the cell. To the two sides are clamped the cathode assemblies, each consisting of a cath-

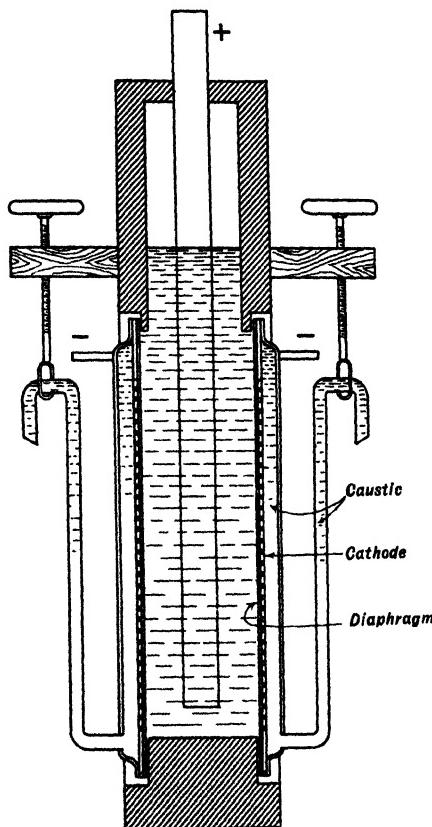


FIG. 121. Giordani-Pomilio chlorine-caustic cell.

ode, a built-up diaphragm, and an outer cover, as shown in the installation in Fig. 122. Artificial graphite electrodes enter through the top of the cell.

The standard size of the cell¹¹ is 3,000 amp., but some smaller and some larger cells are also made. The voltage is 3.5 to 4 volts per cell; the cathodic current density, 43 amp. per sq. ft. The current efficiency is 95 per cent; the energy efficiency, 55 to 60 per cent. The yield is 0.78 lb. caustic and 0.68 lb. chlorine per kw-hr.

¹¹ Personal communication, 1938, Dr. V. Costanzi, London.

Basel Cell. The Basel cell¹³ (also spelled Basle) is not used in the United States; the largest plant using it is the Societa Italiana di Electrochimico, at Bussi, Italy. The cell utilizes the propulsive action of the evolved hydrogen to circulate the electrolyte from the anode to the cathode. For a description of the cell the reader is referred to other sources.¹⁴ It is a submerged-cathode cell.

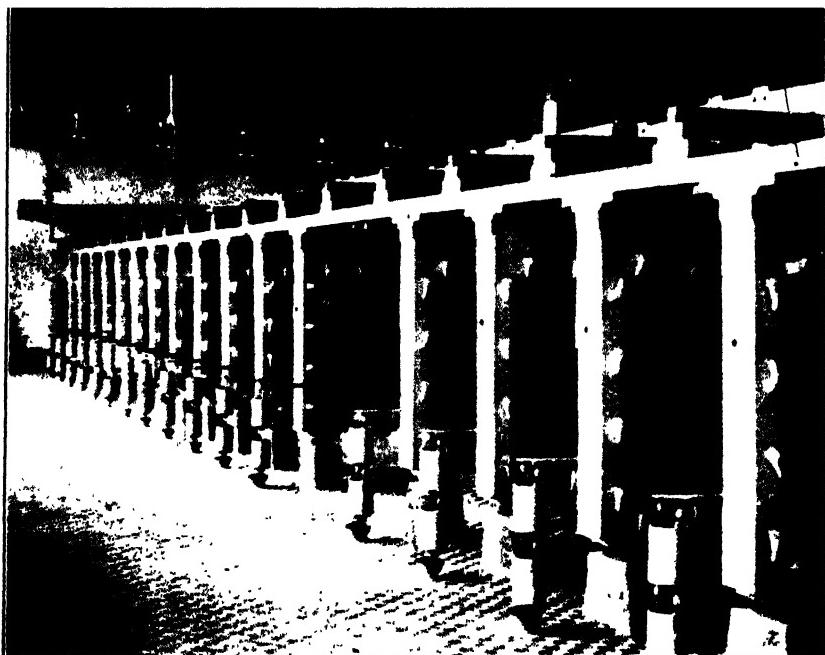


FIG. 122. An installation of Giordani-Pomilio cells.

Hargreaves-Bird Cell. The Hargreaves-Bird cell differs from the other types of cells in that the cathode effluent is a sodium carbonate solution instead of a sodium hydroxide solution. The cell shown in section in Fig. 123 consists of a cast-iron box 10 ft. long, 5 ft. high, and 2 ft. wide, lined on the bottom, ends, and roof with acid-proof bricks laid up with a cement mortar. Two parallel cathodes, each supporting a diaphragm, divide the cell longitudinally into three compartments. The middle or anode compartment contains the anodes of retort carbon; the other two are the cathode compartments. The diaphragms supported by the cathodes are made of asbestos paper, the pores of which

¹³ Gesellschaft für Chemische Industrie in Basel, Improvement in the electrolysis of aqueous solutions, British Patent 11,872, Sept. 18, 1913.

¹⁴ J. B. C. Kershaw, *Chem. & Met. Eng.*, 24, 169 (1921).

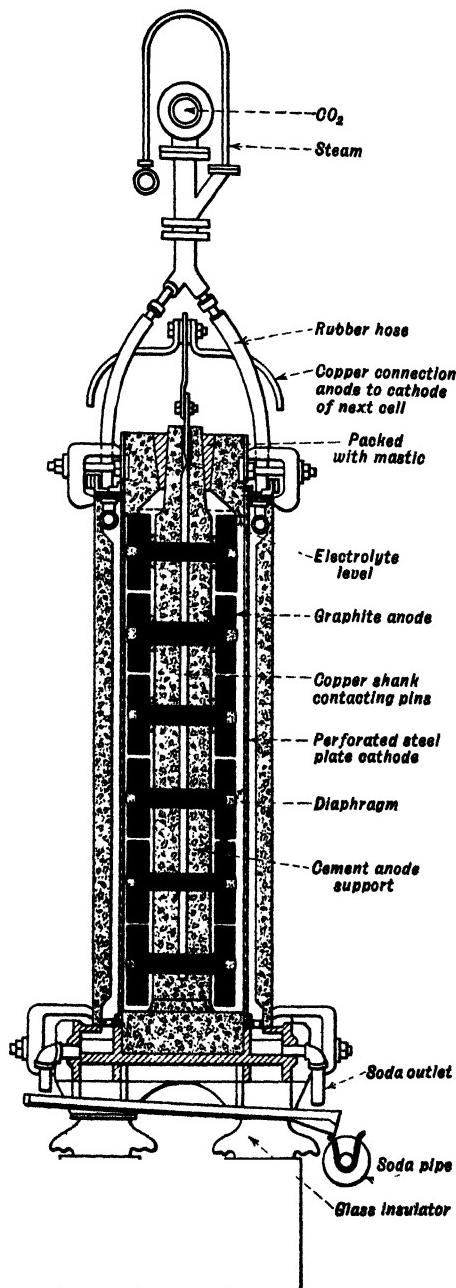


FIG. 123. Hargreaves-Bird cell for producing chlorine and sodium carbonate. (Courtesy West Virginia Pulp and Paper Company.)

have been filled with hydrated calcium silicate, and are of the un-submerged type. The cathodes are made of perforated steel or copper sheet, or wire gauze. Steam and carbon dioxide are blown into the top of the cathode compartment, washing the caustic down the cathode and converting it into sodium carbonate. In this compartment in the earlier cells copper strips were placed horizontally to act as baffle plates to



FIG. 124. Hargreaves-Bird cell room. (*Courtesy West Virginia Pulp and Paper Company.*)

deflect the incoming steam and carbon dioxide against the cathodes. The brine solution enters through a pipe at the bottom of the cell and out an overflow pipe at the top. The brine leaving the cell is brought back to its original concentration and pumped back into the cell.

The advantage of this type of cell over those producing caustic is that, in converting the caustic to sodium carbonate, OH^- ions are removed about as fast as they are formed and there is therefore little chance of any formation of hypochlorite. The cell also has exceptionally long life. The chief disadvantage for general use is that low-priced sodium carbonate is made instead of the more valuable sodium hydroxide.

The cell takes 2,000 to 3,100 amp. at 3.3 to 4.5 volts, the average being about 4.2 volts. The current efficiency is about 92 per cent; the energy

efficiency, 51 per cent. This corresponds to 1.91 lb. sodium carbonate and 0.64 lb. chlorine per kw-hr. The cathode effluent contains 170 g. sodium carbonate and 3.6 g. sodium chloride per liter.

The Hargreaves-Bird cells are used by the West Virginia Pulp and Paper Company. An installation of cells is shown in Fig. 124. Some of the cells operated from 1906 to 1927 without replacement, which is a record probably not duplicated by any other type of cell.

All the cells thus far discussed use vertical diaphragms. The next two cells mentioned have horizontal diaphragms.

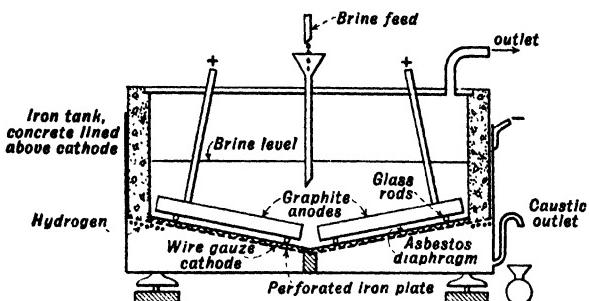


FIG. 125. Le Sueur chlorine-caustic cell. (Courtesy Brown Company.)

Le Sueur Cell. The Le Sueur cell is of special interest because in 1893 it was the first porous-diaphragm cell in operation for the commercial production of chlorine and caustic soda in the United States. It is a submerged-horizontal-diaphragm cell. This type, with some modifications, is still giving satisfactory service at Berlin, New Hampshire. The cathode, an iron wire screen, rests on a perforated metal plate for support. The diaphragm is made of asbestos paper resting on the cathode and cemented to the concrete side walls. The anodes, of Acheson graphite, are separated from the diaphragm by resting on glass rods which hold them about an inch above the diaphragm. The cover is of slate and is cemented onto the top to make a gas-tight compartment above the anode liquor. Small graphite lead-in rods project through the cover to carry the current to the anodes. The negative leads are connected to the iron tank.

Billiter Horizontal Diaphragm Cell (Billiter-Siemens Cell). In the Billiter¹⁵ cell concrete cell walls are placed on an iron tray. The cathode is composed of closely woven iron netting supported horizontally a short

¹⁵ J. Billiter, *Z. Elektrochem.*, 23, 327 (1917).

distance above the floor and connected to it electrically. On the cathode netting is placed a layer of asbestos cloth, and on this is spread a mixture of long-fibered asbestos and barium sulphate. The asbestos serves to make the barium sulphate layer firmer, and, if the sulphate crystals are of the proper size, the combination offers little resistance to the current. Such a diaphragm properly prepared is said to give excellent service. Above the diaphragm is placed a series of 9 graphite anodes. A concrete cover closes the cell at the top, through which pass the anodes, the brine feed, heating pipes, and chlorine outlet. The brine percolates through the diaphragm and then out the bottom of the cell.

Each cell takes a current of 2,500 amp. at 3.5 volts. At a working temperature of 90° C. (192° F.) the cell produces a solution containing about 150 g. sodium hydroxide or 190 g. potassium hydroxide per liter.

Billiter horizontal-diaphragm cells were formerly used by the Niagara Alkali Company, Niagara Falls, New York, but they have been replaced by cylindrical vertical-diaphragm cells. The Billiter cell is not now used in America but is employed in several plants in Germany.

Bell-Jar Cells

No bell-jar cells are used in the United States and they find but limited application in Europe. The chief representative of this type is the Aussig cell.

Aussig Cell. An assembly of 21 cells or bells is shown in one large container in Fig. 126. One of the individual bells is shown in section in

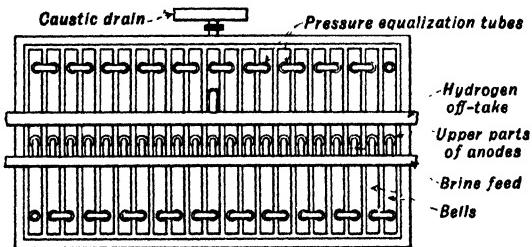


FIG. 126. Aussig bell-jar type chlorine-caustic cells.

Fig. 127. The graphite anode is placed horizontally and is attached to a vertical tube which conducts the current to the anode and also serves as the brine feed. This brine feed is connected to a cross-pipe placed horizontally above the anode. In the upper part of the pipe are a number of small holes; this permits a gentle entry of the brine into the cell. In the newer types of cells the vertical brine feed is a separate pipe

placed near to but independent of the electrical conductor, with the horizontal distributing pipe attached to it. Openings in the cover are connected to U-tubes, which equalize the pressure in all the cells; this is important to prevent surges of the chlorine gas which would disturb the quiet layers of the electrolyte.

The cathode is of sheet steel and really forms the bell. It is lined on the inside with cement which acts as an insulator and protects the jar against corrosion.

A unit of 21 cells is about 4 ft. wide and 10 ft. long. A unit takes 300 amp. (4 amp. per sq. dm. [37.2 amp. per sq. ft.]) which is very

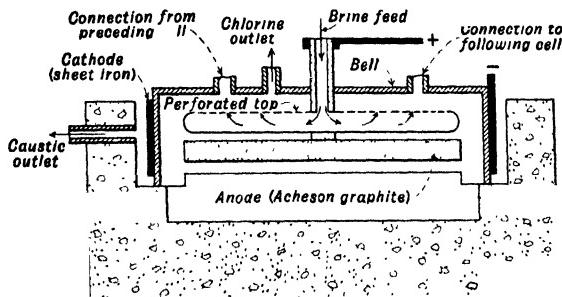


FIG. 127. Vertical section through an individual bell, Aussig cell.

small compared with other types of chlorine-caustic cells. The current efficiency is 85 to 92 per cent. The voltage for a unit begins at 3.7 and rises to 4.2 volts. The cathode alkali contains 130 g. sodium hydroxide or 150 g. potassium hydroxide per liter when saturated brine is used. The best working temperature seems to be about 35° C. (95° F.).

This type of cell is used at Aussig, Czechoslovakia, and in several places in Germany.

Mercury Cells

Castner Cell. In the Castner cell the mercury forms an intermediate electrode. The cell consists of a slate box 4 ft. square and 6 in. deep. It is divided by two slate partitions into three compartments as shown in Fig. 106, page 291. The partitions do not extend quite down to the floor level, and a small groove is cut in the floor under each partition. Mercury is placed in the cell and extends into all three compartments by passing beneath the partitions. The two end compartments contain the graphite anodes and the brine solution. In these chambers the brine is decomposed electrolytically, and the liberated sodium is dissolved in the mercury which serves as cathodes in these compartments. In the middle compartment the mercury serves as anode, and suspended above

the mercury is an iron grid cathode. This compartment contains the caustic solution which is formed by the sodium leaving the mercury and immediately combining with the water.

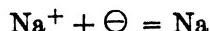
Each end compartment contains, in addition to the anode, a chlorine outlet, a brine inlet, and brine outlet. The brine enters the cell at a concentration of 30 per cent sodium or potassium chloride. This is reduced to 20 per cent in its passage through the end compartments. It leaves these compartments and passes to a concentrating tank, where the sodium chloride content is brought up to 30 per cent. Any sodium sulphate, calcium salts, and iron salts must be removed from the brine. Sulphate ions if permitted to accumulate destroy carbon anodes; ferric hydroxide will settle on the mercury, become reduced to metallic iron, and then produce hydrogen evolution by letting the sodium combine with water in the anode compartment. Calcium and magnesium salts cause increased amalgam decomposition.

The middle compartment is provided with a water inlet and a hydrogen and a caustic outlet.

In the passage of the current through the cell, chlorine is liberated in the outer compartments according to the equation:



and sodium is liberated according to the equation:



The sodium does not combine directly with water to form sodium hydroxide and hydrogen, but dissolves in the mercury in the mercury cathode, mainly as NaHg_4 . The electrolysis in the outer chambers does not take place with 100 per cent efficiency, as was explained in an earlier part of this chapter.

Since the cathodic efficiency in the outer brine compartments is less than 100 per cent, some of the current would have to leave the mercury in the middle compartment in some other way than by forming Na^+ ions. The result is that some of the current that enters the middle compartment forms Hg^+ ions unless some preventive means are provided. This formation of mercurous ions is avoided in practice by shunting part of the current around the middle compartment. The amount of current so shunted is equal to that which would be used in the formation of Hg^+ ions; in commercial practice it amounts to about 10 per cent.

The sodium leaving the mercury in the middle compartment and combining with the water involves a decrease in free energy. This results in a saving of voltage, for the actual voltage applied across the terminals

of the cell is equal to that required to decompose the sodium chloride in the outer compartments minus that generated in the middle compartment. The total e.m.f. across the cell is 4.1 to 4.2 volts.

One might expect that sodium entering the mercury in the outer compartment would diffuse toward the middle compartment. This is true, but the rate of diffusion of sodium in undisturbed mercury is too low for commercial work. It was explained in an earlier part of this chapter that the sodium concentration in the amalgam must be kept low in order to avoid liberation of hydrogen. Sodium amalgam containing appreciable amounts of sodium becomes viscous, and this further reduces the rate of diffusion. In practice the sodium content of the amalgam is kept below 0.2 per cent. In order to facilitate the diffusion of the sodium in the mercury, the cell is rocked mechanically. One end is pivoted as shown in the illustration, and the other end is raised and lowered by a cam about an inch each minute.

Each cell takes 630 amp. at 4.2 volts and has a current efficiency of 90 to 95 per cent. The energy efficiency is about 50 per cent. The yield, based on the current efficiency and operating voltage, is 0.71 lb. sodium hydroxide and 0.65 lb. chlorine per kw-hr.

The solution from the middle compartment contains about 240 g. sodium hydroxide per liter. This illustrates one of the advantages of mercury electrode cells, namely, the high alkali concentration compared with diaphragm or bell-jar cells. Furthermore, the salt concentration in the alkali is nil. Each cell requires a little over 100 lb. of mercury, which makes the capital invested per cell high compared with some other types of cells not using mercury. Against this must be balanced a saving in evaporation cost of the more concentrated caustic solution.

The foregoing is based on early descriptions of the cell.¹⁶ No information is available on the present construction or operation, except that the cell as now used is basically as described, with a number of improvements and refinements added.

Sorensen Cell. The Sorensen cell¹⁷ is a mercury cell but differs from the Castner cell in that no part of the applied current passes into the oxidizing compartment; instead, a local couple is set up between the sodium-mercury alloy, the sodium hydroxide solution, and graphite in the oxidation chamber. In this respect it follows its predecessor, the Whiting cell,¹⁸ which was used for many years and is still employed to some extent.

¹⁶ J. W. Richards, *Electrochem. Ind.*, 1, 12 (1902).

¹⁷ E. Sorensen (Oxford Paper Company), Electrolytic cell, U. S. Patent 1,613,966, Jan. 11, 1927.

¹⁸ J. Whiting, *Trans. Am. Electrochem. Soc.*, 17, 327 (1910).

The construction of the cell is shown in Fig. 128. The cell consists of a decomposing compartment and an oxidizing compartment. In the decomposing compartment the sodium chloride is decomposed electrolytically, the chlorine escaping and the sodium forming an alloy with the mercury cathode. The mercury cathode is a horizontal sheet of mercury at the bottom of the compartment, about 275 lb. mercury being

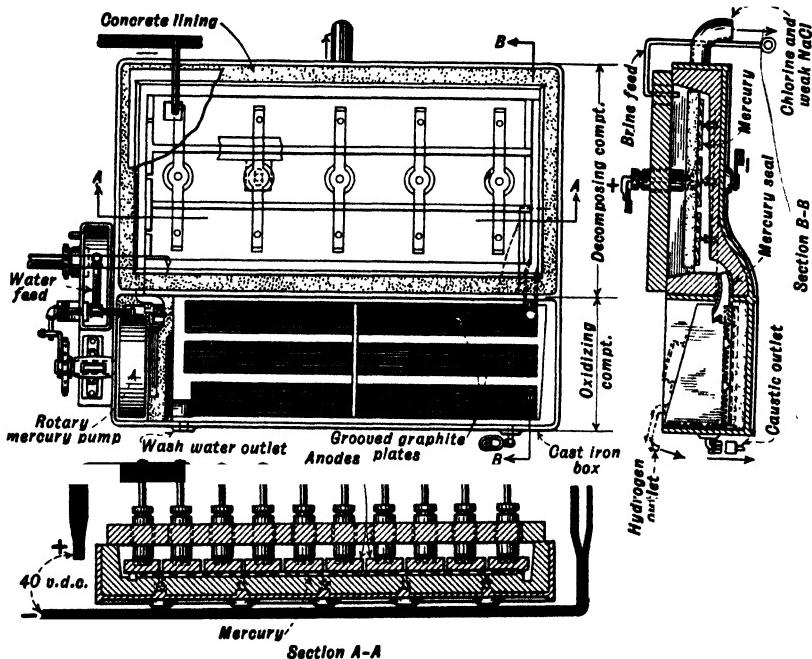


FIG. 128. Sorensen chlorine-caustic cell.

required per cell. The brine is continually introduced through a pipe, is denuded of part of its sodium chloride content, and then leaves the cell carrying with it as a froth the liberated chlorine. The chlorine is separated, and the sodium chloride content of the solution is brought up to the required concentration and recirculated through the cell.

The mercury in the bottom of the cell gradually flows into the oxidizing compartment or denuder, at a lower level, where it comes in contact with graphite plates which form the bottom of the compartment. The compartment is filled with a sodium hydroxide solution. The graphite plates contain grooves and ridges, and the amount of amalgam on these plates is such that both the graphite ridges and the mercury are exposed to the sodium hydroxide solution. A local couple is formed, and the sodium leaves the amalgam and enters the solution as sodium

hydroxide with the liberation of hydrogen. The mercury flows to the lower end of the compartment as it gradually loses its sodium. A rotary pump elevates the denuded mercury, which continuously flows back into the decomposing compartment.

The sodium hydroxide solution leaves the cell through an overflow. A mechanical water feed supplies the proper amount of water, equal to

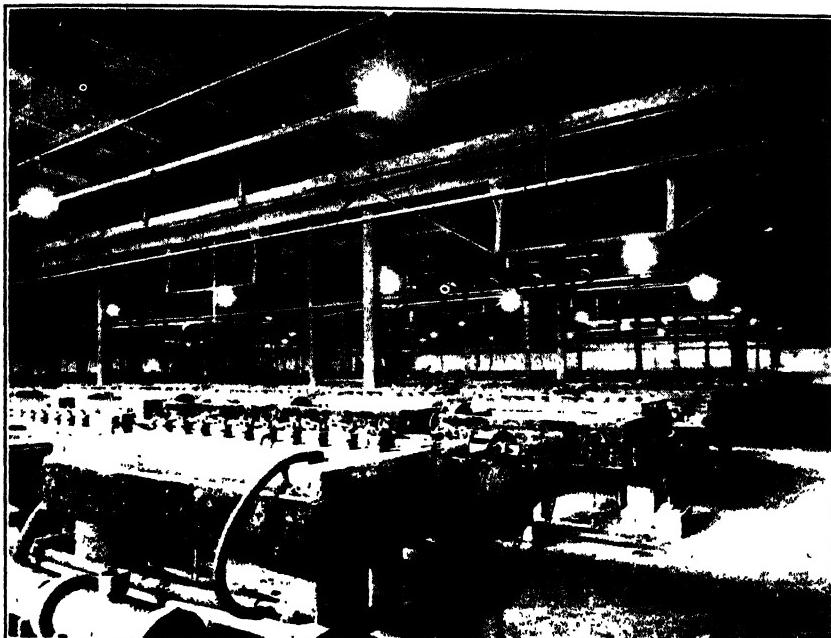


FIG. 129. An installation of Sorensen chlorine-caustic cells. (*Courtesy Oxford Paper Company.*)

that removed by the sodium hydroxide solution. This amounts to about 2.3 gal. per hr. Figure 129 shows an installation of Sorensen cells at the plant of the Oxford Paper Company, Rumford Falls, Maine.

Each cell takes 1,300 amp. at 4.0 volts. The current efficiency is 90 per cent, the energy efficiency 51.8 per cent, which corresponds to 0.74 lb. sodium hydroxide and 0.66 lb. chlorine per kw-hr. The cathode alkali contains about 205 g. sodium hydroxide per liter and is free from sodium chloride.

The greater bulk of chlorine is made by the electrolysis of sodium chloride solutions, but other methods are also used. Some is obtained in the electrolysis of fused chlorides discussed in Chapter IX. Chlorine is also produced chemically by the well-known Weldon and Deacon processes. A large part of the caustic soda produced is prepared chemically

by the sodium carbonate-lime process. More recently an electrolytic method has been developed for producing chlorine from hydrochloric acid in an electrolysis cell known as the Low-Vorce acid cell. The cell has carbon anodes and a copper cathode, and it operates at 2.1 volts with a current efficiency of 95 per cent or above.

Chlorine is also produced by The Solvay Process Company at Hopewell, Virginia, as a by-product in its nitrogen-fixation plant. The process involves the production of chlorine and sodium nitrate from salt and nitrogen.

Disposition of Cell Products

Packaging and Transportation of Chlorine. The chlorine from electrolysis cells is very pure. In nearly all types of cells the purity of the chlorine produced is above 97 per cent. In some places all the chlorine is used at the plant for making bleaching powder; this is particularly true at paper mills. In others, part of the chlorine is consumed at the plant, or is piped directly in stoneware mains to consumers located near by. However, a great deal of chlorine is shipped in liquid form. Pure dry chlorine will not attack steel, so that steel is universally used for containers. The chlorine, therefore, after it leaves the electrolysis cells is passed against 66° Bé. sulphuric acid which removes the moisture.

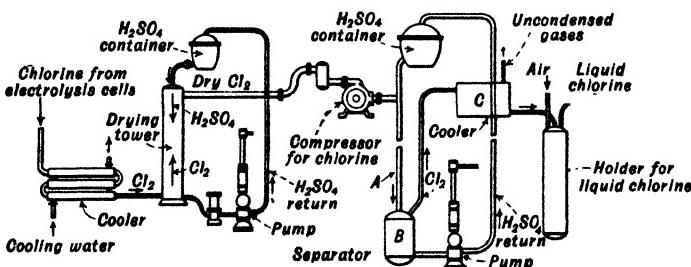


FIG. 130. System for condensing gaseous chlorine to liquid chlorine.

The chlorine to be shipped is compressed and cooled to form liquid chlorine. The boiling point of chlorine is -33.6° C. (-28.5° F.), but by compression it can be liquefied at a higher temperature. Chlorine can be liquefied under a variety of temperatures and pressures. One method is to cool the chlorine to a low temperature by means of carbon dioxide. It then requires a pressure of but a few pounds to liquefy the chlorine. Another method is to use brine as a refrigerant. The brine is cooled by direct expansion of ammonia, which gives a temperature of -20° to -27° C. (-4° to -17° F.). This requires a pressure of 30 to 45 lb. per sq. in. to liquefy the chlorine. It is also possible to liquefy the chlorine

with water as the cooling medium if pressures in the neighborhood of 100 lb. per sq. in. are used. Figure 130 shows schematically a system used on this continent for liquefying chlorine. The wet chlorine as it comes from the electrolysis cells is cooled by water and is then dried in a tower where it rises against a falling spray of sulphuric acid. The dry chlorine passes on to a compressor where it is compressed to a pressure



FIG. 131. Nash Hytor turbo compressors for chlorine. (*Courtesy Hooker Electrochemical Company.*)

of about 22 lb. per sq. in. A falling stream of sulphuric acid in pipe *A*, which is 4 in. in diameter and 100 ft. long, further compresses the chlorine to 100 lb. per sq. in. In separator *B* the chlorine is separated from the acid and then passes to the cooler *C* where it is cooled and liquefied at -25°C . (-13°F). An installation of chlorine compressors is shown in Fig. 131.

Chlorine is usually shipped in steel cylinders of 100- or 150-lb. capacity. The pressure in the cylinders varies with the temperature as shown on the following page.

Liquid chlorine is also shipped in tank cars. Nearly a thousand tank cars are in use in the United States for the transportation of liquid chlorine. Single-unit tank cars carry 16 tons and 30 tons net; multiple-

unit tank cars carry 15 containers, each container holding 1 net ton of chlorine.

The chlorine in containers is in liquid form but is drawn off as a gas. When the pressure in the cylinders is released, the Joule-Thomson

CHLORINE GAS PRESSURE IN CYLINDERS

Temperature ° C.	Temperature ° F.	Gage Pressure, lb. per sq. in.
-16	4	12
0	32	39
20	68	82
45	104	148
60	140	242
80	176	402
100	212	598

effect acts to cool the chlorine, and consequently diminishes the pressure to such an extent that large volumes of gas cannot be drawn off. Therefore, if it is desired to maintain a large continuous flow of gas, the cylinders should be set in a container in which there is about 15 in. of water at not above 60° C. (140° F.); each cylinder contains a fusible safety plug that melts at 70° C. (158° F.). When the cylinder valve is closed the hot water must, of course, be removed to prevent excessive pressure in the cylinders.

Chlorine can be withdrawn from a cylinder as a liquid by inverting the cylinder and supporting it at an angle of 30° to the ground.

Production and Uses of Chlorine. The first commercial electrolytic production of caustic and chlorine was in Germany in 1890, and it was not until several years later that commercial production was begun in the United States. In 1942 there was produced in the United States approximately 910,000 tons of electrolytic caustic soda compared to 625,000 tons by the lime-soda process, and 850,000 tons of chlorine coincident with the sodium hydroxide. In addition, probably over 100,000 tons of chlorine was produced electrolytically in the manufacture of metallic sodium and caustic potash.

The largest proportion of chlorine is used by the paper mills for bleaching paper pulp. It oxidizes the organic coloring matter, mainly lignin, which was not completely removed during the cooking and washing. For this purpose, as well as for many other bleaching operations, the chlorine is run into a tank containing a suspension of hydrated lime, $\text{Ca}(\text{OH})_2$, forming bleaching powder, $\text{CaCl}(\text{OCl})$,



This is generally referred to as a "bleach liquor." Bleaching powder is employed in many bleaching operations, including the bleaching of textiles and shellac. It is used in the sterilization of municipal water supplies and the treatment of sewage. In late years liquid chlorine has replaced bleaching powder to a considerable extent for various industrial bleaching and oxidizing operations. It is utilized directly in the sterilization of water, the chlorination of ores, and the manufacture of chemicals.

In the petroleum industry, chlorine in the form of sodium and calcium hypochlorites is used in place of the "doctor solution" in the sweetening of gasoline and kerosene. As aluminum chloride, AlCl_3 (which is made by treating aluminum metal with chlorine, or a mixture of bauxite and carbon with chlorine), it helps to break down the long-chain hydrocarbons into shorter ones, thus producing gasoline and kerosene by "cracking." Ethylene glycol, $\text{CH}_2\text{OHCH}_2\text{OH}$, which has wide application today as an anti-freeze for automobile cooling systems, is prepared by treating ethylene, C_2H_2 , with hypochlorous acid, HClO , which is itself prepared from chlorine. The reaction produces chlorhydrin, from which the ethylene glycol is prepared by hydrolysis with sodium bicarbonate.

Practically all detinning of scrap tin plate is done by treating the dry and clean metal scrap with dry chlorine gas. The chlorine forms stannic chloride,



which is collected as a liquid; the detinned iron scrap can be remelted.

Chlorine has also been employed with some success as a cure for diseases of the respiratory tract. The uses of chlorine are so numerous that a complete list would not be possible in a work of this sort, and the reader is referred to other sources for more complete discussions.

Caustic. The concentration of the cathode alkali differs in different types of cells and also varies according to operating conditions. In mercury cells the cathode alkali generally contains 25 per cent or more caustic soda and substantially no sodium chloride. In diaphragm cells the caustic content may vary between 8 and 16 per cent and the salt content between 10 and 16 per cent.

The customary practice is to evaporate the caustic liquor obtained from the cells in vacuum pans or evaporators. These may be single, double, or triple effect depending upon the size of the plant. An installation of caustic evaporators is shown in Fig. 132. For the evaporators use is made of nickel tubes, nickel or nickel-armored steam chests, and nickel or nickel-clad vacuum pans and pumps. The sodium chloride is less soluble than the caustic soda, and as evaporation proceeds the sodium chloride crystallizes and settles to the bottom. The salt and

some caustic liquor are removed; the salt is separated, and the caustic liquor is returned to the evaporator. The removed salt when washed free from caustic is exceptionally pure, for not only is the brine purified before it enters the cell, but also any foreign materials not completely removed in the preliminary treatment are retained in the cell. Angel¹⁹ has described a method of washing and removing this salt in a pure condition.

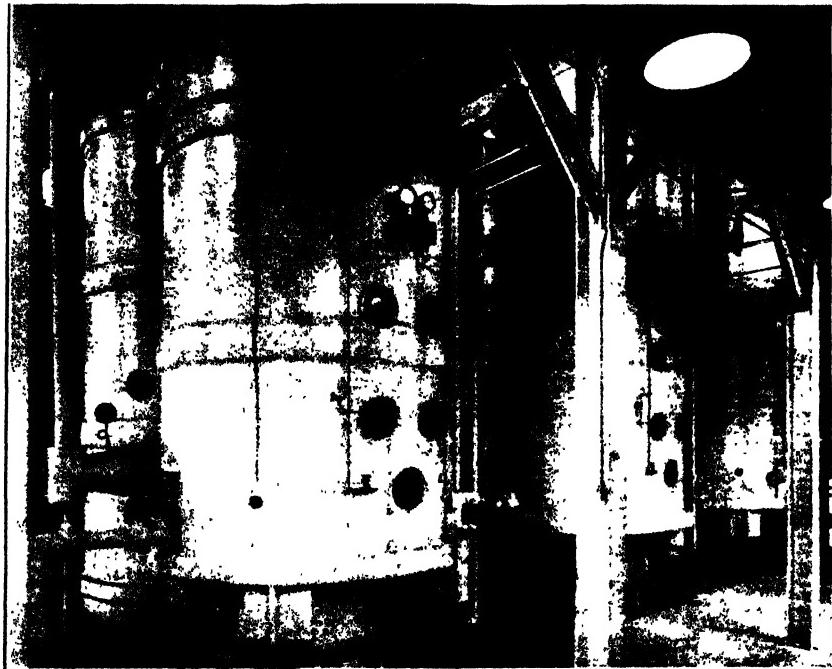


FIG. 132. Caustic evaporators. (*Courtesy Hooker Electrochemical Company.*)

The purified salt has a market value of more than three times that of the rock salt used for the brine. The concentrated solution is further evaporated in a single-effect evaporator where it is concentrated to a caustic content of 50 per cent and a small amount of salt. When this solution passes through a cooling apparatus more salt crystallizes, but the salt content formerly could not be reduced below 16 or 17 g. per liter by evaporation. Much of the caustic is marketed as a strong caustic solution containing 50 to 55 per cent sodium hydroxide. It is shipped in tank cars or in 55- or 110-gal. steel drums.

If it is desired to reduce the salt content further, the 50 per cent strong liquor is slightly diluted so that it becomes unsaturated with

¹⁹ G. Angel, *Chem. & Met. Eng.*, **33**, 746 (1926).

respect to sodium chloride. It is then cooled until the caustic but not the salt crystallizes. The caustic crystals are filtered free from salt and are finished as solid sodium hydroxide.

Usually the 2 per cent or less of sodium chloride is not objectionable. Therefore, the strong caustic liquor is run into large cast-iron pots for evaporation to dryness. These pots are 10 ft. in diameter and 6 ft. deep and are heated by coal, oil, or gas. When all the water has been evaporated and the caustic lies in a quiet molten state, sulphur is added to clarify the liquid, which consists mainly in the removal of iron. The molten caustic is run into steel drums holding about 740 lb. each.

The strong liquor may also be passed over flaking drums for producing flake caustic.

More recently it has become the practice to remove the salt by the addition of sodium sulphate to the strong caustic liquor, forming a triple salt, $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{NaOH}$. The resulting caustic is practically free from salt and compares favorably with caustic soda produced in mercury cells.²⁰

The last few years has seen a great increase in the production and shipment of liquid caustic soda. Much more caustic soda is now shipped as liquid of 50 and 70 per cent and higher concentration than is shipped as fused caustic in steel drums. The solution is shipped in tank cars heavily insulated in order to keep the solution hot to prevent crystallization. Large quantities of caustic soda solution are being transported on the Pacific coast in oil tankers on their return trips. The Mathieson Alkali Works has a specially designed tank boat for the transportation of high-grade caustic liquor in nickel-lined compartments.²¹

Hydrogen. It has in the past been the practice in most plants to waste the hydrogen to the atmosphere, or in some to burn it as fuel under the evaporators. Lately the tendency has been to use some of the hydrogen and an equivalent amount of chlorine to produce synthetic hydrochloric acid at the chlorine-caustic plant, or to utilize the hydrogen in other ways.

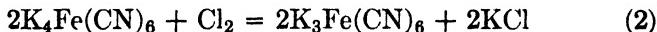
²⁰ D. A. Pritchard, *Trans. Electrochem. Soc.*, **65**, 16 (1934).

²¹ R. L. Murray, *Trans. Am. Inst. Chem. Engrs.*, **36**, 454 (1940).

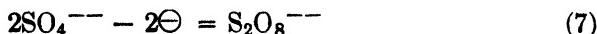
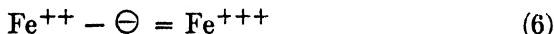
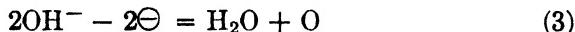
CHAPTER XI

ELECTROLYTIC OXIDATION AND REDUCTION¹

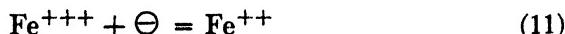
Oxidation and reduction reactions involve more than reaction with oxygen on the one hand and with hydrogen or a metal on the other. Chlorine is a very common and convenient oxidizing agent, as is shown by the following equations in which oxygen and chlorine each oxidize potassium ferrocyanide to ferricyanide,



In electrolysis cells, all reactions at the anode are oxidizing reactions and those at the cathode are reducing reactions. The following reactions are typical electrolytic oxidization reactions. It will be observed that each reaction involves the loss of one or more electrons.



The following equations represent reduction reactions at the cathode; it will likewise be observed that in each there is a gain of one or more electrons.



¹ It is strongly urged that Chapter XII, "Depolarization and Electrolysis," of Vol. I, be read in connection with this chapter.

In the discussion of electrochemical oxidation and reduction reactions in this chapter, only those processes will be considered in which products are made at the anode or cathode alone. Those reactions in which anode and cathode products combine to form a final product are not called oxidation or reduction processes; and, in a still narrower sense, we are largely concerned with oxidation reactions in which oxygen or chlorine liberated at the anode oxidizes some material to produce a new compound, or with reduction reactions in which hydrogen liberated at the cathode reduces some material to give a new product.

As pointed out in Vol. I, Chapter XII, the principal types of electrolytic oxidation involve the discharge of hydroxyl ions or of halogen ions as represented by equations 3 and 4. Electrolytic reduction involves the discharge of hydrogen ions, equation 9, followed by the interaction of the nascent hydrogen and the material to be reduced.

The substances to be reduced or oxidized act as depolarizers; i.e., electrolytic oxidation or reduction are depolarizing processes. Therefore, the liberation of free hydrogen at the cathode during a reducing process represents a loss in efficiency. It is consequently desirable to select cathodes with a high hydrogen overvoltage, or anodes with a high oxygen or halogen overvoltage. It has been shown that substances like pyridine and compounds containing the keto group can be reduced readily with cathodes having a high overvoltage, like lead and mercury, but not with a platinum cathode.² The materials suitable for anodes for oxidation processes are much more limited than those suitable for cathodes for reduction processes. In Vol. I, Creighton points out that:

Since, in general, it is important that the anode should be attacked as little as possible during electrolysis, we are confined to the use of platinum, iridium, palladium, carbon, iron, and nickel for processes which take place in alkaline solution, and to the platinum metals and carbon for those which are carried out in acid solution. Anodes of lead dioxide may be employed in sulphuric acid solutions. Of these anodes, iron and nickel have the lowest oxygen overvoltages. For general work, the most suitable anodes are: (1) lead, for sulphate solutions; (2) Acheson graphite, for chloride solutions; and (3) pure nickel or a high nickel-steel, for alkaline solutions.

Catalysts may also play an important role in electrolytic oxidation and reduction by increasing the efficiency of oxidation or reduction reactions. Catalysts may be added in small quantities to the catholyte, or the cathode itself may act in that capacity. As an illustration of the first case, it was pointed out in Vol. I that quinone may be reduced to hydroquinone at a platinum cathode if a small quantity of titanium chloride is present. As an illustration of the second case may be cited the fact that potassium nitrate is more easily reduced at an iron cathode

² J. Tafel, *Z. physik. Chem.*, **30**, 187 (1900); *Ber.*, **33**, 2209 (1900).

than at a platinum or zinc cathode. This is because potassium nitrate is a more efficient depolarizer at an iron cathode than at zinc or platinum electrodes.

Catalysts in common use in electrolytic oxidation processes are cerium, mangano, titanium and vanadium salts, and ferricyanides and chromates.

However, the catalytic action of the cathode may also have a negative effect on the efficiency. Hydrogen overvoltage is due to monatomic electrically neutral hydrogen at the cathode, and it occurs most strikingly with those metals which have the least catalytic action on the reaction



A low current density also promotes more complete reduction, for a high current density decreases the concentration of the depolarizer in the vicinity of the cathode. Large cathode surfaces are therefore desirable.

Many compounds have been prepared electrochemically. A list of a large number of compounds has been prepared by Swann,³ in which are listed the starting materials, products, yield percentages by weight, with references to the original literature. This list should be consulted by all interested in electro-organic chemistry.

Reduction of Organic Compounds. Only a few electrolytic processes for the oxidation of organic compounds have found commercial application, although many have been described in the literature.⁴ The same may be said regarding electrolytic reduction of organic compounds.

Organic compounds are poor conductors so that for their electrolysis it is necessary to add an electrolyte. In some cases it is the electrolyte that is decomposed by the electric current and the nascent electrode products combine with the organic compound which is suspended or dissolved in the electrolyte. In many cases, but not in all, it is necessary to use a diaphragm to maintain a separate anolyte and catholyte.

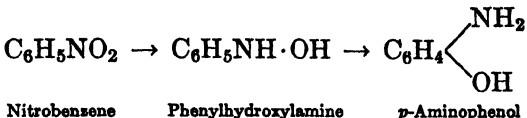
Para-aminophenol was made in the United States during the first World War.⁵ Nitrobenzene in a 91 per cent sulphuric acid solution was used as catholyte. A diaphragm of unglazed porcelain separated the catholyte from an 82 per cent sulphuric acid solution as anolyte. The current density on the platinum cathode was 28 to 37 amp. per sq. ft. (3 to 4 amp. per sq. dm.) at 8 volts. The working temperature of the cell

³ Sherlock Swann, Jr., *Trans. Am. Electrochem. Soc.*, **69**, 287 (1936); **77**, 459 (1940).

⁴ See, for instance, C. J. Brockman, *Electro-Organic Chemistry*, John Wiley & Sons, New York, 1926.

⁵ A. S. McDaniel, L. Schneider, and A. Ballard, *Trans. Am. Electrochem. Soc.*, **39**, 441 (1921).

was 30° C. (86° F.). The nitrobenzene is reduced to phenylhydroxylamine, which is converted to *p*-aminophenol by intramolecular change:



The sludge of sulphate and sulphonate produced in the cell was treated with hydrochloric acid; the *p*-aminophenol chloride obtained was purified. The yield was 40 to 50 per cent; the current efficiency, 25 per cent.

Mannitol and Sorbitol from Glucose. A commercial process for the electrolytic reduction of sugars to polyhydric alcohols has been developed by Creighton.⁶ The process is used especially for the manufacture of sorbitol and mannitol. Mannitol is of particular importance in the explosives industry; both compounds can serve as the starting material for the synthesis of new organic compounds and are used in large quantities. Glucose is a suitable raw material, and it is available in large quantities at low cost. The sugar is reduced to its corresponding alcohol in alkaline aqueous solution which is made conducting by the addition of a suitable electrolyte, such as sodium sulphate; sodium hydroxide is added to make the solution alkaline.

Each cell contains 36 amalgamated lead cathodes and 35 lead anodes suspended alternately in a tank 13 ft. long, 6 ft. wide, and 3 ft. deep. Each anode is completely surrounded by an Alundum diaphragm.

During the electrolysis the temperature of the catholyte is kept down by circulation through cooling coils. At the conclusion of the electrolysis the catholyte passes on to a vacuum kettle where the water is evaporated and the residue of mannitol, sorbitol, and sodium sulphate is digested with hot ethyl alcohol to dissolve the alcohols. The undissolved sodium sulphate is separated from the hot solution by filtration. The alcoholic filtrate passes to a crystallizer where it is cooled sufficiently to cause the mannitol to crystallize. The mass of crystals and mother liquor is separated in a basket-type centrifuge, and the separated mannitol crystals are purified by recrystallization from water.

The alcoholic solution from the centrifuge is evaporated, and the resulting thick syrup of sorbitol is purified by treatment with activated charcoal. The treated sorbitol syrup contains about 15 per cent water and small amounts of glucose and sodium sulphate. The syrup can be further purified, or crystalline sorbitol can be separated from it.

⁶ H. J. Creighton (Atlas Powder Company), Process for electrolytically reducing sugars to alcohol, U. S. Patent 1,612,361, Dec. 28, 1926; and U. S. Patent 1,990,582, Feb. 12, 1935; H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939); R. L. Taylor, *Chem. & Met. Eng.*, **44**, 588 (1937).

Hydrogen Peroxide. For many years hydrogen peroxide was produced electrolytically by an anodic process in which persulphuric acid or persulphates were formed from sulphuric acid or sulphates or bisulphates. Three such processes which have been in use many years have been developed to a satisfactory degree of efficiency: the Weinstein or du Pont process, the Pietsch and Adolph process, and the Löwenstein process. In all three processes persulphuric acid, $H_2S_2O_8$, or persul-

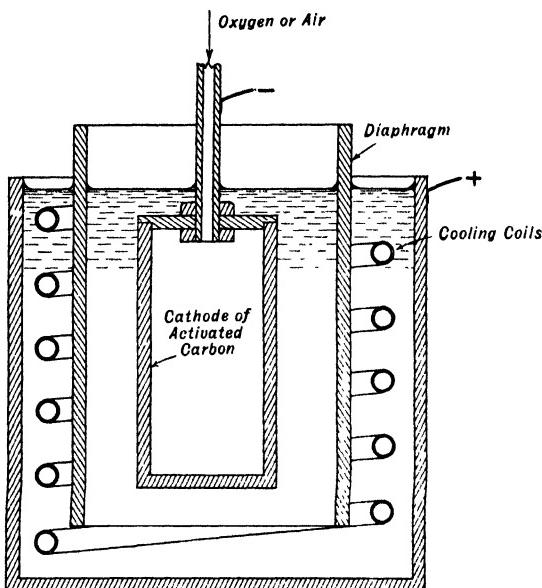


FIG. 133. The Berl cell for production of hydrogen peroxide.

phates are formed electrolytically from which hydrogen peroxide is formed by saponification with the formation of Caro's acid, H_2SO_5 , as an intermediate product.

Berl⁷ has developed a process based on the direct formation of an alkaline salt of hydrogen peroxide at the cathode from which hydrogen peroxide can be obtained by distillation. The cell used is shown diagrammatically in Fig. 133. The electrolyte may be an aqueous solution of a variety of alkali salts or hydroxides. The anode product will therefore vary, depending on the nature of the electrolyte. The electrolyte, however, must be alkaline. Potassium compounds give better yields than the corresponding sodium compounds.

The cell container serves as anode, and if alkali hydroxides or carbonates are used and oxygen is liberated at the anode the anode should

⁷ E. Berl, *Trans. Electrochem. Soc.*, **76**, 361 (1939).

preferably be made of nickel. The cathode is made of activated carbon, for which the water-soluble acid sludge from oil refineries is a very satisfactory raw material. The sludge is neutralized with potassium compounds and then carbonized by heating. If potassium salts are used as the electrolyte the potassium salt of hydrogen peroxide is formed in the cathode compartment:



The hydrogen is obtained by direct discharge of hydrogen ions; the oxygen is obtained from the air, which can be enriched with oxygen from the anode reaction. An electrolyte containing 500 g. per liter of KOH will produce a concentration of 250 g. per liter of H_2O_2 .

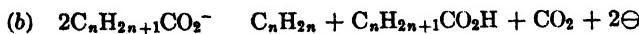
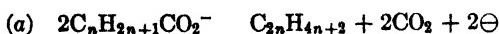
It is not possible to distil off the hydrogen peroxide from the alkaline peroxide solution. The electrolyte is diluted with a mineral acid, e.g., hydrochloric acid, to a pH below 7. Hydrogen peroxide can then be distilled off with practically no loss since neither persulphuric acid nor Caro's acid is present to decompose the peroxide.

The current yield is 0.543 kw-hr. per lb. of 30 per cent H_2O_2 , which is three times the yield of the older anodic process. The current efficiency is better than 90 per cent.

Aten⁸ has given a résumé of the application of electrolytic reduction, including many organic compounds. Other examples are mentioned in Vol. I, pp. 281 to 283.

Oxidation of Organic Compounds. Practically all the reactions taking place during electrolysis of organic compounds occur at the anode, for, with the exception of the relatively small number of organic bases, the cations of organic electrolytes do not usually take part in any reaction at the cathode. As further stated by Creighton:⁹

Although oxygen is usually produced at the anode when dilute solutions of aliphatic monobasic acids or their salts are electrolyzed, with concentrated solutions and a high current density, in general, union takes place between the discharged anions, which is followed by a splitting off of carbon dioxide from the new molecule. The different types of reactions which may occur under these conditions are represented by the following equations:



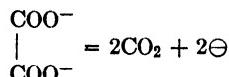
Which one of these reactions takes place depends largely upon the nature of the anion and but slightly upon the experimental conditions. With potassium acetate,

⁸ A. H. W. Aten, *Chem. Weekblad*, 19, 349 (1922).

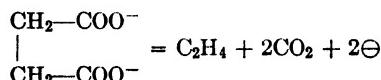
⁹ Vol. I, p. 286.

ethane and carbon dioxide are formed; with the salts of propionic and butyric acids the anode reaction corresponds to (b); with trichloroacetic acid reaction (c) predominates. As a rule, the salts of aromatic monobasic acids yield only oxygen at the anode.

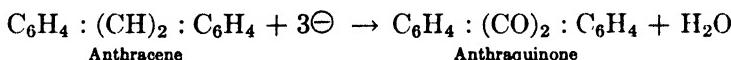
Electrolysis of salts of dibasic acids results merely in oxidation and not in synthesis. For example, with potassium oxalate, carbon dioxide is the sole product formed at the anode:



while with an alkaline succinate the anode products are ethylene and carbon dioxide:



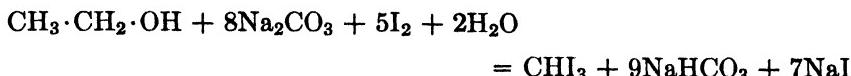
Anthracene, $C_6H_4 : (CH)_2 : C_6H_4$, can be oxidized electrolytically to *anthraquinone*, $C_6H_4 : (CO)_2 : C_6H_4$. For electrolysis the anthracene is suspended in sulphuric acid and the mixture is used as anolyte employing a platinum anode. If no catalyst is used the efficiency is low, there is liberation of much oxygen, and the anode potential is high. Catalysts commonly used are ceric sulphate, $Ce(SO_4)_2$, or chromic acid, $H_2Cr_2O_7$. Either catalyst gives up part of its oxygen, and the oxygen combines with the anthracene:



The catalysts are reduced in the process to $\text{Ce}_2(\text{SO}_4)_3$ or $\text{Cr}_2(\text{SO}_4)_3$ respectively but are regenerated to their original oxidizing condition by the anodic action of the current. Ceric sulphate is such a rapid oxidizer that there is no danger of its cathodic reduction as long as anthracene is present, even without the use of a diaphragm. The cerous sulphate, $\text{Ce}_2(\text{SO}_4)_3$, is therefore regenerated in the electrolyzer. Chromic acid, however, reacts more slowly so that the spent liquors are drawn from the electrolyzer, regenerated electrolytically elsewhere, and returned to the cycle.

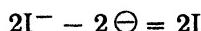
The electrolyzer is a lead-lined container which acts as anode; the electrolyte contains 20 per cent sulphuric acid with 2 per cent ceric sulphate. During the electrolysis the temperature rises from 70 to 100° C. (158 to 212° F.). With an anodic current density of 5 amp. per sq. dm. at 3 volts the current efficiency is nearly 100 per cent. Cerous sulphate is colorless, and owing to the rapidity of the depolarization the solution remains colorless until the finish of the oxidation of the anthracene to anthraquinone, after which the yellow color of the ceric sulphate becomes manifest. No diaphragm is used in the cell.

Iodoform, CHI_3 , is prepared commercially by electrolytic oxidation. It can also be formed chemically without electrolysis by the interaction of alkali and either alcohol or acetone with iodine. In the chemical method the iodine is added at 60 to 70° C. (140 to 158° F.) to an aqueous alcoholic solution containing sodium carbonate. The equation is



The yield, however, is only about 25 per cent, for most of the iodine is combined as sodium iodide, NaI . In the electrolytic method the yield is 98 per cent.

In the electrolytic process the first stage consists in the formation of IO^- ions.



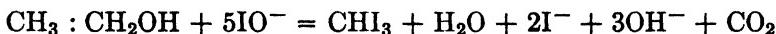
then



The IO^- ion then reacts with the alcohol or acetone to form the iodine substitution product. With acetone the reaction is expressed by the equation:



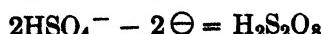
with alcohol this net change can be expressed by the equation:



Information is not available on the present-day method of producing iodoform, but the method developed by Foerster and Meves¹⁰ is simple and works very well in the laboratory. Their electrolyte consists per liter of 50 g. sodium carbonate, 170 g. potassium iodide, and 100 g. 96 per cent alcohol. The anode is smooth platinum, the cathode lead, which is surrounded by a diaphragm of parchment paper. The cell operates at about 65° C. (149° F.) with a current density at the anode of 1 to 2 amp. per sq. dm. at 2 to 2.5 volts. The crystals of iodoform when washed are very pure.

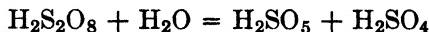
Chloroform and *bromoform* can likewise be prepared electrolytically.

Oxidation of Sulphate to Persulphate. Persulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, is prepared commercially by the electrolysis of sulphuric acid. The exact reactions involved in the formation of persulphuric acid have not been definitely established. In its simplest form it may be considered the result of the discharge of HSO_4^- ions:

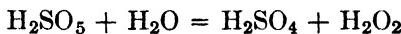


¹⁰ F. Foerster and W. Meves, *Z. Elektrochem.*, 4, 268 (1897).

The persulphuric acid is not very stable in the presence of sulphuric acid, and changes to Caro's acid, H_2SO_5 ,



Caro's acid then further decomposes to form hydrogen peroxide, H_2O_2 ,



The last two equations show the reactions taking place in the commercial production of hydrogen peroxide.

The rate of decomposition of the persulphuric acid depends upon the concentration of the sulphuric acid. Sulphuric acid of sp. gr. 1.35 to 1.45 gives maximum yield of persulphuric acid. The yield also increases with current density. Until a current density of 25 amp. per sq. dm. is reached the yield increases very rapidly to about 55 per cent at $10^\circ C.$ ($50^\circ F.$). Beyond that this yield increases more slowly with increases in current density, and at 600 amp. per sq. dm. the yield is about 70 per cent. The temperature also has an important bearing on the yield, which decreases with rise in temperature. At $60^\circ C.$ ($140^\circ F.$) the persulphuric acid decomposes as rapidly as it is formed so that the yield is zero. Therefore, cooling of the anodes increases the current efficiency. The presence of small quantities of sulphates such as ammonium, aluminum, nickel, and potassium and chlorine and fluorine ions also increases the yield.

Smooth platinum anodes give best results; palladium and platinized platinum give no yield at all. The cathodes used in commercial practice consist of lead, which may be the tank lining itself or special shapes which permit water cooling. The electrolyte is a saturated solution of purified ammonium sulphate, either alone or slightly acidified with sulphuric acid. The cells require either a diaphragm or an addition of 0.2 per cent of potassium dichromate or potassium chromate, $K_2Cr_2O_7$ or K_2CrO_4 , to the electrolyte to decrease reduction of the persulphate at the cathode. The electrolyte may be cooled either by means of lead cooling coils serving as cathode, or by continuously circulating the electrolyte so that it may be cooled outside the cell. In the second method the ammonium persulphate, $(NH_4)_2S_2O_8$, formed is removed continually as the electrolyte is circulated.

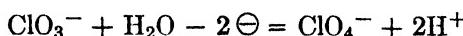
The current density ranges from 325 to 465 amp. per sq. ft. (35 to 50 amp. per sq. dm.) at the anode. The e.m.f. is 6 to 7 volts per cell. The operating temperature is $30^\circ C.$ ($86^\circ F.$) as a maximum. The tanks are made of chemical stoneware or of wood or cement, lead lined.

Oxidation of Chlorates to Perchlorates. Potassium and ammonium perchlorates, $KClO_4$ and NH_4ClO_4 , are used in the manufacture of fire-

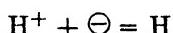
works and explosives. Their importance lies in the fact that they easily give up oxygen to promote rapid combustion. Both salts are prepared by double decomposition between sodium perchlorate and potassium chloride or ammonium chloride. The sodium perchlorate is not used directly in explosives because of its deliquescent properties, but it is prepared electrolytically because of the greater solubility of sodium chlorate than of either potassium or ammonium chlorates.

If the anode potential is sufficiently high the oxidation of the ClO_3^- ion to the ClO_4^- ion occurs with a high current efficiency. It is necessary, therefore, to use smooth platinum electrodes; if platinized, oxygen is evolved and the yield falls. With anodes of iron oxide, Fe_3O_4 , no chlorate is formed even under conditions that would otherwise be most favorable.

The anode reaction¹¹ can be represented by



and the cathodic reactions as



In practice, a concentrated solution of perhaps 60 to 70 per cent sodium chlorate, NaClO_3 , is electrolyzed without a diaphragm between smooth platinum anodes and iron cathodes. The required anode potential may be obtained by either operating at a low temperature, 10° C. (50° F.) or lower, or by operating at a higher temperature of 30 to 60° C. (86 to 140° F.). At the higher operating temperatures, current densities of 280 to 465 amp. per sq. ft. (30 to 50 amp. per sq. dm.) at the anodes are used as against 75 amp. per sq. ft. at the lower temperature. The high-current-density method has supplanted the low-current-density method.

Operating data of cells have been published by Williams¹² and by Knibbs and Palfreeman.¹³ The cells described by Williams began a run with about 418 to 465 amp. per sq. ft. (45 to 50 amp. per sq. dm.) at the anodes, at 30° C. (86° F.), and finished at 50 to 60° C. (122 to 140° F.) with a current density of 280 amp. per sq. ft. (30 amp. per sq. dm.). At the close of a 6- to 7-hr. run, the chlorate was reduced from 650 g. per liter to 5 g. per liter. The current efficiency was above 85 per

¹¹ The actual mechanism of the anodic process is in dispute. For a fuller discussion of possible anode reactions see A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, p. 487, Edward Arnold and Company, London, 1924.

¹² J. G. Williams, *Trans. Faraday Soc.*, **15**, 134 (1920).

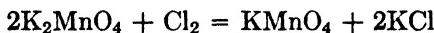
¹³ N. V. S. Knibbs and H. Palfreeman, *ibid.*, **16**, 402, 424 (1921).

cent. The oxygen evolved toward the end of the run contained much ozone. The figures given by Knibbs and Palfreeman are similar to the above.

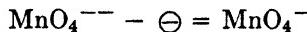
Oxidation of Manganate to Permanganate. Potassium permanganate, $KMnO_4$, is prepared from potassium manganate, K_2MnO_4 , which, in turn, is prepared by fusing together manganese dioxide and potassium hydroxide in the presence of air which produces the manganate according to the equation:



The manganate is dissolved, filtered, and oxidized to permanganate. The oxidation may be by chemical or electrolytic means. In the chemical method the manganate is treated with chlorine and sulphuric or carbonic acid, which oxidizes it to permanganate:



It will be observed that in the oxidation due to the carbon dioxide one-third of the manganese is changed back to manganese dioxide, and two-thirds of the potassium originally used is converted into carbonate. These losses are avoided by electrolytic oxidation of the leach from the alkaline roast. The reaction at the anode may be represented by



The electrolysis is carried out in non-diaphragm cells. Reduction of the permanganate at the cathode is kept low¹⁴ by using a high cathodic current density; i.e., the cathode surface is made small compared to the anode surface. The technical cells consist of iron vessels containing iron rods as cathodes and sheet-iron anodes. The areas of the electrodes are such as to give anodic and cathodic current densities of 84 and 840 amp. per sq. ft. (9 and 90 amp. per sq. dm.), respectively. The bath contains 9 per cent potassium manganate and 5 per cent potassium hydroxide, and is worked at 60° C. (140° F.). The cells are operated at about 3 volts; the current efficiency is about 70 per cent, which corresponds to 0.32 kw-hr. per lb. of potassium permanganate. The losses are due in part to anodic oxygen evolution, but chiefly to cathodic reduction. Although the efficiency is poor, the cost of power per pound of product is sufficiently low that the older type of diaphragm cells have been supplanted by the non-diaphragm cells.

¹⁴ P. Askenasy, *Tech. Elektrochem.*, 2, 72 (1916).

The electrolyte containing permanganate in suspension is cooled, which causes more permanganate to crystallize. The crystals are removed and the liquor is further concentrated in vacuum evaporators.

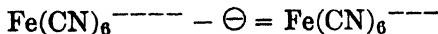
Permanganate can also be prepared by the anodic solution of ferromanganese in an alkaline electrolyte, first demonstrated by Lorenz.¹⁵ The iron in the anodes is oxidized and forms a Fe(OH)_3 mud along with some manganese. If the alkali in the electrolyte is potassium hydroxide, an oxide scale collects on the anode which soon forms an insulating coating so that no more metal goes into solution. With carbonate this does not happen if the temperature is not allowed to go much above 40° C. (104° F.). The yield in permanganate increases with the manganese content of the anodes. Under 40 per cent manganese there is no yield;¹⁶ with 75 per cent manganese anodes the yield is about 60 per cent;¹⁷ 2 per cent cobalt in the anode entirely prevents the formation of permanganate.

The current efficiency rises with increase in current density. The minimum energy consumption is at 56 amp. per sq. ft. (6 amp. per sq. dm.), but the higher yield obtained at twice this current density more than balances the small increase in cost of energy.¹⁸ The minimum energy consumption is at 30° C. (86° F.). The current efficiency decreases rapidly with rise in temperature.

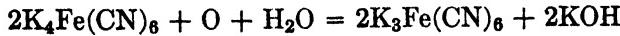
Oxidation of Potassium Ferrocyanide to Ferricyanide. Potassium ferricyanide can be prepared by passing chlorine into the ferrocyanide:



It is now made by electrolytic oxidation; the net anode reaction can be represented by



It is not definitely known whether the oxidation proceeds as above or by the action of discharged oxygen according to the equation



The electrolysis has been studied by v. Hayek.¹⁹ The reaction takes place with a high current efficiency. Additions such as chromate are not efficient in preventing cathodic reduction of the ferricyanide

¹⁵ R. Lorenz, *Z. anorg. Chem.*, **12**, 393 (1896).

¹⁶ R. E. Wilson, W. G. Horsch, and M. A. Youtz, *J. Ind. Eng. Chem.*, **13**, 763 (1921).

¹⁷ M. de K. Thompson, *Chem. & Met. Eng.*, **21**, 680 (1919).

¹⁸ M. de K. Thompson, *Theoretical and Applied Electrochemistry*, p. 260, Macmillan Company, New York, 1925.

¹⁹ H. v. Hayek, *Z. anorg. Chem.*, **39**, 240 (1904).

formed, so that a diaphragm is necessary. Brown²⁰ and his associates conducted experiments with cells with and without diaphragms. Without diaphragms the current efficiency did not exceed 50 per cent; with diaphragms it was near 100 per cent.

Grube²¹ used a cell with an unglazed porcelain diaphragm. The anode materials used, nickel, copper, platinum, iron, and lead peroxide, had no effect on the yield. The anolyte was a potassium ferrocyanide, $K_4Fe(CN)_6$, solution; the catholyte was either a half-saturated ferrocyanide or potassium hydroxide solution. The current efficiency was practically 100 per cent until oxygen evolution commenced. Dilute solutions were completely oxidized at room temperature with about 90 per cent current efficiency when using 4.65 amp. per sq. ft. (0.5 amp. per sq. dm.).

Regeneration of Chromic Acid. Chromic acid, $H_2Cr_2O_7$, is used as an oxidizing agent in the preparation of a number of organic compounds, e.g., in oxidation of anthracene to anthraquinone previously discussed in this chapter, and in the manufacture of camphor and organic acids. In some cases the chromic sulphate, $Cr_2(SO_4)_3$, resulting from the reduction of chromic acid, is thrown away; in others it is regenerated by electrolytic oxidation and used over.

A spent solution requiring regeneration may contain 390 g. chromic sulphate and 350 g. sulphuric acid per liter. The solution is electrolyzed in a lead-lined tank, using lead electrodes. Although for a given current density the voltage is higher with a smooth platinum anode than with a lead anode in a chromic acid-sulphuric acid solution, the reaction does not take place on smooth platinum anodes. The reaction with lead anodes is attributed to a small amount of lead salts in the solution which act as catalysts. The chromic sulphate is oxidized by nascent oxygen liberated electrolytically at the anode. The reaction may be represented by the equation:



The anode becomes coated with lead peroxide. Attempts have been made to use cells without diaphragms,²² but investigators seem to have made more progress by using diaphragms.²³

The current efficiency is 70 to 90 per cent at 3.2 to 3.5 volts. Hydrogen is liberated at the cathode and oxygen at the anode. Sulphate ions migrate to the anode to some extent, which increases the sulphuric

²⁰ O. W. Brown, C. O. Henke, and I. L. Miller, *J. Phys. Chem.*, **24**, 230 (1920).

²¹ G. Grube, *Z. Elektrochem.*, **20**, 334 (1914).

²² P. Askenasy and A. Révai, *Z. Elektrochem.*, **19**, 344 (1913).

²³ R. H. McKee and S. T. Leo, *J. Ind. Eng. Chem.*, **12**, 16 (1920).

acid content of the anolyte. By using the spent liquor as catholyte and causing it to circulate through the diaphragm to the anode compartment, and by adjusting the rate of flow, LeBlanc succeeded in obtaining a continuous regeneration undisturbed by changes in the sulphuric acid concentration.

White Lead. White lead is manufactured electrolytically at the plant of the Anaconda Lead Products Company in Indiana by the Sperry

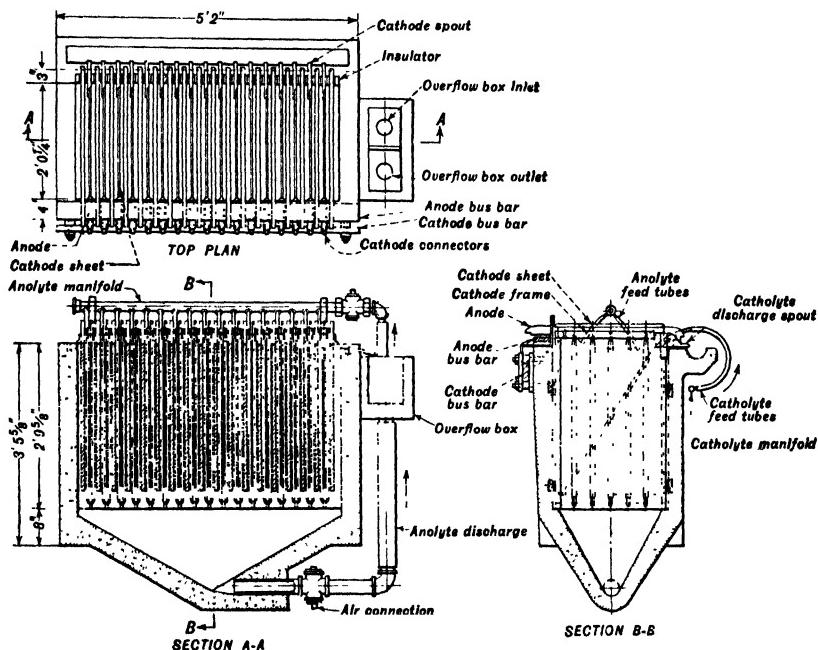


FIG. 134. Section of an electrolysis cell for the production of white lead.

process described by Bowman.²⁴ The process consists essentially of electrolyzing a lead acetate solution in a cell with lead anodes and iron cathodes. A cell is shown in section in Fig. 134. The cell proper consists of a rectangular tank with hopper bottom, built entirely of reinforced concrete ("gunnite"). The cells are $24\frac{1}{4}$ by 54 by $33\frac{5}{8}$ in., inside, with walls 3 in. thick, reinforced with wire mesh. The discharge is connected through an inverted siphon to an overflow box of concrete placed at one end of the cell. The cell and the overflow box are lined with asphalt enamel to prevent penetration of the concrete by the solution with consequent corrosion of the reinforcement.

The anodes are rectangular lead plates 21 by $30\frac{1}{2}$ by 1 in. and weigh 250 lb. each. Projecting lugs for supporting the anodes in the cell are

²⁴ R. G. Bowman, *Trans. Am. Inst. Mining Met. Engrs.*, 73, 146 (1926).

cast at the two upper corners of the anodes in a manner resembling those on anodes for copper refining, except that they have a larger section on account of the lower physical strength of the lead. The anodes



FIG. 135. Installation of electrolysis cells for the production of white lead. (*Courtesy Anaconda Lead Products Company*)

hang in the cell, supported by their lugs, one lug of each anode resting on a block of hard rubber on the rim of the cell, the other on the anode bus-bar.

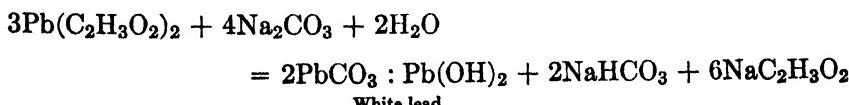
The cathodes are sheets of 16-gage steel plate. They are encased in envelopes of heavy, tightly woven linen duck, which act as diaphragms. By means of specially constructed cathode frames the

diaphragms are supported so that they are parallel between the anodes and cathodes, but make direct contact with neither. There are 18 anodes and 19 cathodes to a cell. An installation of cells is shown in Fig. 135. The electrolyte consists of an anolyte and catholyte each kept separate from the other except as they meet at the diaphragms. The two solutions each contain approximately 4 per cent sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$. In addition the anolyte contains from 0.06 to 0.2 per cent sodium carbonate and approximately 0.05 per cent sodium bicarbonate.²⁵ The catholyte is the feeder solution and may contain as much as 5 per cent sodium carbonate.

The two electrolytes enter and leave the cells and are circulated throughout the plant in two separate systems, except that proper connections are made for adding small amounts of catholyte to anolyte, or vice versa, to control the concentration of the solutions and to maintain a proper distribution of volumes. The piping system consists of brass or hard rubber for the main lines, fittings, and nipples, connected with lines of pure gum hose. The anolyte is supplied to the cell through a $1\frac{1}{2}$ -in. manifold distributor of hard rubber, supplied with 18 short nipples on each side. Short rubber tubes hang from each nipple and deliver the solution into the cathode compartments without splashing. The rate of flow of the anolyte is 16 to 18 gal. per minute.

The catholyte is distributed to the cells through a system of rubber hose and piping similar to that carrying the anolyte. The rate of circulation of the catholyte is approximately 3.5 gal. per minute.

During the electrolysis the lead is dissolved at the anode electrolytically. The anolyte in the immediate vicinity of the anode contains sodium acetate, so that a lead acetate solution is formed. As the lead acetate diffuses away from the anode it meets sodium carbonate as the result of the CO_3^{--} ions passing through the diaphragm from the cathode compartment by electrical migration. White lead is precipitated, which may be represented by the probable equation:



The basic lead carbonate, called white lead, settles to the bottom of the cell and is carried from the cell as a suspension in the anolyte. It passes through hard-rubber-lined launders to a sump. From there the anolyte carrying approximately 0.5 per cent white lead in suspension is pumped to a Dorr thickener, from which it leaves as a pulp containing

²⁵ Private communication from Mr. R. G. Bowman, East Chicago, Indiana.

20 per cent solids. The white lead from the thickener is washed and filtered in Moore vacuum filter and then dried at a maximum temperature of 120° C. (248° F.).

The clear anolyte leaving the thickener is pumped back to the electrolytic cell. In warm weather it is cooled in a copper-tube heat exchanger using city water as a cooling medium. The anolyte enters and leaves the cell at the same chemical composition; there is no decomposition or fouling of the solution in the process.

The spent catholyte discharged from the tanks is pumped to carbonating towers where it is restored to its original composition and is returned to the catholyte feed tank. The carbonating towers are concrete shafts 8 by 8 by 21½ ft. high inside, lined with steel. The solution is sprayed from the top of the towers against a rising stream of carbon dioxide, made by burning coke in a deep bed in a furnace. The gas is drawn through a wet cyclone collector in which dust, soot, and traces of sulphur dioxide are removed. It then rises through tile-filled towers, duplicates of the carbonating towers, where any remaining moisture and dust are collected. A fan then delivers the gas to the three carbonating towers. The gas averages 12 per cent carbon dioxide by volume.

The following operating data are given by Bowman:

New anode weight, lb.	250
Scrap anode weight, lb.	75
Time of corrosion, hr.	85
Cell voltage	3.50
Current density, amp. per sq. ft.	29.60
Current efficiency, per cent	97.0
Anolyte temperature, °C.	40.0
Thickener feed, per cent solids	0.50
Thickened pulp, per cent solids	30.
Washed filter cake, per cent solids	55.
Dried product, per cent moisture	0.20
Dryer temperature, maximum, °C.	120.

The outstanding characteristics claimed for electrolytic white lead are exceptional purity and uniformity, extreme fineness of grain, and brilliant whiteness. It finds extensive use as a pigment in paints and as an ingredient in certain glazes.

Other Oxidation Processes. A large number of electrolytic oxidation processes have been developed, only a few of which have attained commercial acceptance. Some have possibilities and may find practical

[redacted] by the electrolytic oxidation of sulphur
[redacted] of sulphide ores has been studied

by Thompson and his associates.²⁶ It is suggested that the sulphur dioxide might be used to depolarize unattackable anodes in the extraction of copper and similar operations. The sulphur dioxide is oxidized to sulphuric acid.

Cadmium yellow has been produced electrolytically²⁷ in a two-compartment cell. Sticks of electrolytic cadmium acted as anode, steel as cathode, and a weakly acid solution of an alkali sulphide was used as electrolyte. Ferrous sulphite, FeS, dissolved in the cathode compartment served as the source of sulphur; the iron remained in a finely divided state as a by-product. The cadmium sulphide, CdS, was precipitated in the anode compartment, which made a pigment of a brilliant and permanent yellow color.

Manganese dioxide can be made by electrolyzing a solution of manganese sulphate at 84 to 158 amp. per sq. ft. (0.9 to 1.7 amp. per sq. dm.) with current efficiencies of over 90 per cent.²⁸

The production of chlorates and hypochlorites is discussed in Chapter X, "The Electrolysis of Alkali Halides."

²⁶ M. de K. Thompson, N. J. Thompson, and A. P. Sullivan, *Met. Chem. Eng.*, **15**, 677 (1916); **18**, 178 (1918).

²⁷ C. G. Fink and W. M. Grosvenor, Jr., *Trans. Am. Electrochem. Soc.*, **58**, 475 (1930).

²⁸ G. D. van Arsdale and C. G. Maier, *ibid.*, **33**, 109 (1918).

CHAPTER VII

HYDROGEN AND OXYGEN

Hydrogen and oxygen are produced electrolytically on a large scale in this country and abroad. Over 200 electrolytic plants are operating in the United States, about one-half of which are run by private industrial users for making their own gases.

All commercial oxygen is obtained either by liquefaction of air, followed by fractional distillation, or by electrolysis of a sodium hydroxide or potassium hydroxide solution. Hydrogen is prepared commercially by a greater variety of processes. The following sources are available for commercial hydrogen: (1) Water gas; the gas contains about 50 per cent hydrogen and 43 per cent carbon monoxide. On treatment with steam under proper conditions the carbon monoxide and water combine to form hydrogen and carbon dioxide, so that the converted gas contains 52 per cent hydrogen, 45 per cent carbon dioxide, and 3 per cent carbon monoxide. The carbon dioxide is removed by washing with water under high pressure followed by a sodium hydroxide treatment. The carbon monoxide is removed by scrubbing with cuprous ammonium formate. (2) Coke-oven gas; the gas contains about 55 per cent hydrogen. The hydrogen is removed by liquefaction and fractional distillation. (3) By-

product in the corn fermentation industry for the production of butanol.

(4) *Some natural gas is very high in its hydrogen content.* (5) *By passing steam over finely divided iron.* Commercially the resulting iron oxide is then reduced with some cheap reducing gas, such as water gas, and is used again. (6) By-product from chlorine-caustic cells. (7) Electrolysis of water.

The relative importance of the various sources of hydrogen for ammonia manufacture may be observed in the following table, which gives the annual consumption of hydrogen in the manufacture of synthetic ammonia in all countries in 1930.¹

	TONS
Water-gas hydrogen	256,600
Coke-oven hydrogen	103,100
Electrolytic hydrogen	67,000
Electrolytic by-product hydrogen	3,300

¹ W. P. Howard, in H. A. Curtis, *Fined Nitrogen*, p. 473.

For the consumption of electrolytic hydrogen in synthetic ammonia manufacture for the same year, Italy came first, Japan, France, Switzerland, Spain, Sweden, and the United States following in the order given. However, in addition large amounts of hydrogen are used in welding and cutting, hydrogenation of oils, both vegetable and petroleum, and reduction processes, and for filling balloons. Over 3,000,000 cu. ft. of electrolytic hydrogen are produced annually in the United States.

Oxygen is used for cutting and welding in conjunction with hydrogen or acetylene, and for chemical and medical purposes.

Where both oxygen and hydrogen are required, as for the oxyhydrogen flame used in welding, and cutting and brazing of metals, electrolysis of water is ordinarily the most convenient and economical method for preparing the gases, but there are a number of cases in which oxygen obtained from liquid air is more economical.

Electrolytic oxygen and hydrogen are very pure. Manufacturers of cells guarantee a purity above 99.0 per cent, and in some a purity of 99.9 per cent is attained. The impurity in electrolytic hydrogen is mainly oxygen, and vice versa. Many users of oxygen or hydrogen, or both, find electrochemical preparation advantageous for it offers an outlet for off-peak power. In this connection McMichael² says:

In order to satisfy a peak demand that may be made during only a single hour during the entire year, electric companies must install and maintain generating equipment with capacity at least equal to the maximum requirement that may develop from any possible combination of circumstances or events that can be anticipated. As a consequence, almost all central stations have generating equipment ready to serve, the entire capacity of which will rarely be in service simultaneously as much as 80 hours during the year, or less than 1 per cent of the whole period. . . . Wherever there is use for hydrogen and oxygen either for consumption or sale as such or as essential materials in industrial processes, especially chemical synthesis, such surplus off-peaks energy can be utilized in a highly beneficial manner in electrolytic cells to dissociate water into its component gases.

Cell Construction. Little difficulty is encountered in finding suitable materials for constructing the cell proper. Iron or steel is used for the cell container and piping. Special attention has been given to selecting a material for the electrode surfaces, which should resist corrosion and also have a low oxygen and hydrogen overvoltage. Nickel is a suitable metal for this purpose, and nearly all anodes are iron or steel plated with nickel. The electrodes of the Electrolabs cell are cobalt plated for still greater reduction in overvoltage.

²P. McMichael, *Chem. & Met. Eng.*, 37, 484 (1930).

Most diaphragms are made of pure asbestos cloth, but finely perforated metal ones are also in use. In the early history of electrolytic oxygen-hydrogen cells, attempts were made to use some cotton yarn in the asbestos cloth to increase its mechanical strength, but it was found that the caustic in the electrolyte attacked the cotton sufficiently to make it necessary to use asbestos only.

The voltage required per cell depends upon the reversible decomposition potential of water, which is 1.23 volts at room temperature, the overvoltages of the gases on the electrode surfaces, contact resistances, and

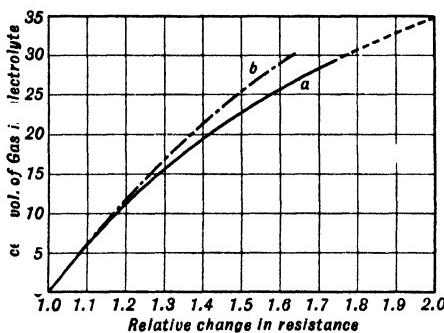


FIG. 136. Increase in resistance of electrolyte due to suspended gas bubbles: (a) measured, (b) calculated.

the ohmic resistance of the electrolyte. This last item depends upon the composition and concentration of the electrolyte, its temperature, and the volume of gas bubbles it contains. The electrolyte ordinarily employed is a 15 per cent sodium hydroxide solution or less commonly a 25 per cent potassium hydroxide solution. The production per kilowatt-hour is about 8 per cent greater with a potassium hydroxide solution, but sodium hydroxide is considerably cheaper and is used more commonly. The relative change in the resistance of the electrolyte with varying volumes of gas bubbles in the electrolyte is shown graphically in Fig. 136.³ The total e.m.f. per cell usually varies from 2 to 2.5 volts. The current efficiency invariably is almost 100 per cent. The raw material for electrolysis is distilled water. Only 3 to 5 per cent alkali is removed with the gas per annum.

Types of Cells. The cells used in the electrolytic production of oxygen and hydrogen may be classified into diaphragm and bell-jar cells, as shown diagrammatically in Fig. 137. Figure 137(a) is a diaphragm cell with separate electrodes; in (b) the cell walls act as electrodes; (c) shows a

³ By permission from V. Engelhardt, *Handbuch der technischen Elektrochemie*, Akademische Verlagsgesellschaft, M.B.H., Leipzig, 1933.

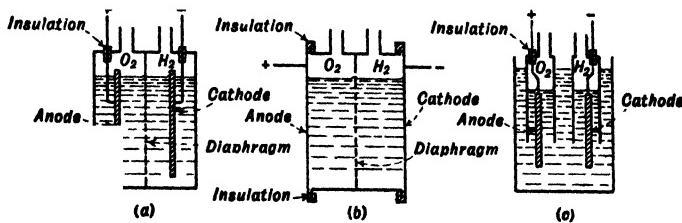


FIG. 137. Different types of cells for producing hydrogen and oxygen electrolytically.

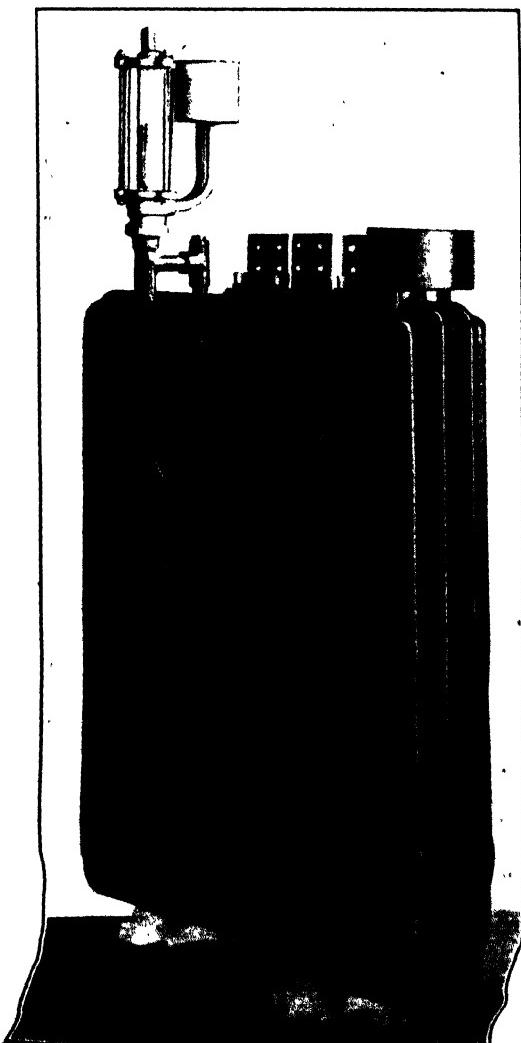


Fig. 138. Electrolabs hydrogen-oxygen cell. (Courtesy Gas Industries Company.)

bell-jar cell. In some bell-jar cells the lower part of the bells have diaphragm extensions.

The cells may also be classified as unit cells, in which each complete unit contains an anode and a cathode or two anodes and a middle

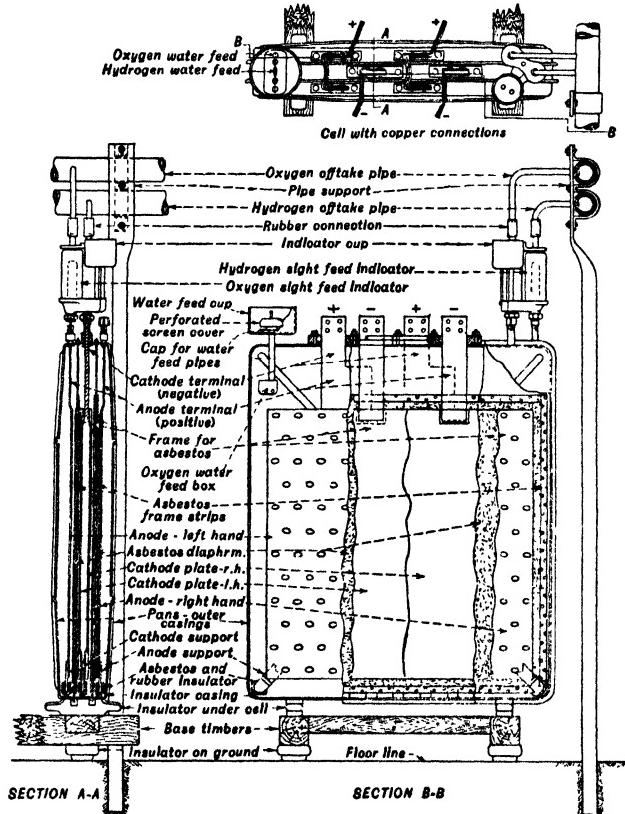


FIG. 139. Structural details of Electrolabs hydrogen-oxygen cell. (Courtesy Gas Industries Company.)

cathode, or as multiple cells, in which a number of electrodes with the necessary diaphragms or bells or both make up a larger unit.

Electrolabs Cell. The Electrolabs cell, also called after its inventor the Levin cell, is of the unit type, manufactured by the Gas Industries Company. A general view of the cell is shown in Fig. 138; the construction is shown in Fig. 139. The cathode is placed centrally with an anode on each side, the electrodes being independent of the casing. Asbestos cloth diaphragms attached to metal frames are placed between the anodes and the cathode. The electrodes are sheet steel. In the earlier

cells the anodes were nickel plated, the cathodes cobalt plated to reduce the overvoltage of the oxygen and hydrogen each to its practicable minimum. In the cells constructed at present, both electrodes are cobalt plated. Each compartment of the cell has an independent water feed so constructed that it serves as a blow-off device to vent the gas under abnormal conditions. A specially designed sight feed indicator is placed between the cell and the gas offtake pipe.

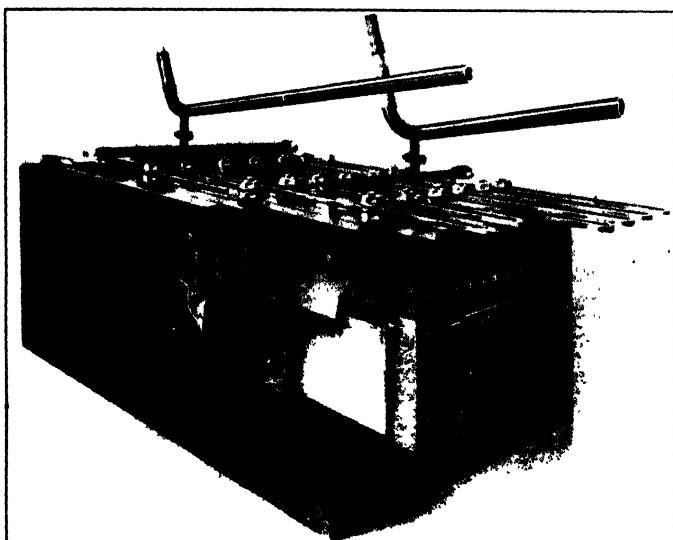


FIG. 140. Sectional view of a Knowles hydrogen-oxygen cell. (*Courtesy The Linde Air Products Company.*)

Cells are manufactured in two sizes. The 250-amp. cell measures 30 by 25 by $6\frac{1}{4}$ in. and produces 2 cu. ft. oxygen and 4 cu. ft. hydrogen per hour. The 600-amp. cell measures 34 by 37 by $8\frac{1}{2}$ in. and produces 4.8 and 9.6 cu. ft. of oxygen and hydrogen per hour, respectively. The two sizes are constructed exactly alike and are delivered entirely welded and assembled. In installations the units are connected in batteries, the electrical connections being in series.

A larger cell is manufactured by the same company. This cell is constructed similarly to the Electrolabs cell and is built in units having capacities of 400 to 2,500 amp.

Knowles Cell. The Knowles cell consists of a sheet-steel tank which contains the anodes and cathodes suspended underneath steel gas-collecting bells, as shown in Fig. 140. The electrodes are of heavy steel plate at least $\frac{1}{8}$ in. thick to prevent warping. The manufacturers have found that if the electrodes are not perfectly flat and parallel to

each other the current concentrates at the high points, which causes rapid corrosion at these points and adversely affects the quality of the gases. The electrodes are hung from the collecting bells, electrically insulated from them, and each electrode is so placed that nearly the whole of the electrode is lower than the bell itself. Asbestos diaphragms surround alternate electrodes and are suspended from the collecting sheet-steel bell above that electrode. They hang down loosely between the electrodes without strain and have an operating life of about 10 years. Hydrogen and oxygen are taken off at the tops of alternate collecting bells.

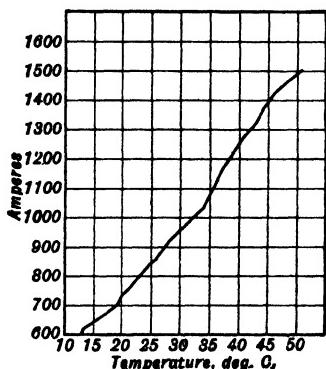


FIG. 141. Current-temperature relation in a Knowles cell at 2.6 volts per cell.

sections in these mains, so that any spray carried with the gases runs back into the cells.

The cathodes are heavy steel; the anodes are steel treated to produce a matte surface and are heavily nickel plated.

The electrolyte consists of an 18 to 20 per cent sodium hydroxide solution or a 25 to 30 per cent potassium hydroxide solution. With the latter the production per kilowatt-hour is a little higher but this advantage is offset by the greater cost of the electrolyte and its greater attack on the diaphragms and insulators, so that ordinarily it is preferable to use sodium hydroxide.

A 3,000-amp. cell is approximately 4 ft. long, $2\frac{1}{2}$ ft. wide, and $2\frac{1}{2}$ ft. deep. It operates at an e.m.f. of 2.125 to 2.25 volts and produces 48.4 cu. ft. of hydrogen and 24.2 cu. ft. of oxygen per hour. The purity of the hydrogen and oxygen is 99.75 and 99.5 per cent, respectively. The current varies directly as the voltage.

The conductivity of the electrolyte increases rapidly with a rise in temperature. This means that as the temperature increases the current rises at constant voltage, as shown graphically in Fig. 141. The voltage-

temperature relation is shown in Fig. 142. The Knowles cell is built so that it can operate between 60 and 65° C. (140 and 149° F.). Coils are placed in each cell and are so arranged that steam, hot water, or cold water can be used to maintain an even temperature in the cell. Temperature control is of value where the electric supply varies, as when working on "off-peak" load. When the electric energy available is low, the cells are heated to maintain their maximum efficiency; when the supply is abundant the cells may be overloaded, in which event the temperatures are kept down by circulating cooling water.

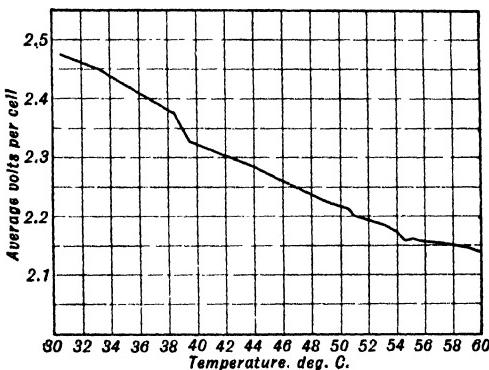


FIG. 142. Voltage-temperature relation in a Knowles cell at 1,000 amp.

Shriver Filter-Press-Type Electrolyzer. The Shriver electrolyzer resembles the well-known recess-plate-type filter press; in fact, it is an adaptation of the filter press, with appropriate modifications in its construction, for the purpose of generating oxygen and hydrogen. It consists essentially of a series of cells formed by cast-iron bipolar electrode plates, which are recessed and separated from each other by rubber-bound asbestos diaphragms. These plates and diaphragms are clamped together tightly by a steel screw actuated by a capstan in a conventional filter press frame, as shown in Fig. 143.

The electrodes on one type are of cast iron, nickel plated, 3 ft. square, and about $\frac{7}{8}$ in. thick. There are 61 plates to an electrolyzer, forming 60 cells in which the gases are generated. Each cell is divided into an anode and a cathode compartment by the diaphragm as indicated in Fig. 144. There are two large holes, one near each upper corner of the plates as shown in Fig. 145, that permit the gases to escape from the cells as generated. At the two lower corners are two more holes through which the return electrolyte, freed from the gases, is supplied to the cells. There are corresponding holes in the diaphragms, and when the electrodes and diaphragms are clamped together the holes coincide to

form channels running the entire length of the electrolyzer in which the gases are carried to large separating tanks located at the head of the machine. There are two of these separating tanks, one for the oxygen and one for the hydrogen. These tanks are designed to separate the gases from the foaming electrolyte, wash the gases on the way out, and

FIG. 143. Shriver hydrogen-oxygen electrolyzer. (*Courtesy T. Shriver and Company.*)

return the electrolyte to the lower channels of the cell. The rising gas bubbles in the cells cause the electrolyte to circulate without any other agency.

At the follower end of the electrolyzer the two electrolyte return channels at the lower corners of the plates are connected for the purpose of balancing the concentration of the electrolyte. If these channels are not connected there is a tendency to build up the caustic concentration on the cathode side. The make-up water, distilled, is added at this point in the system.

The separator tanks are placed at the head end of the machine, as shown in Figs. 143 and 144. If more complete separation is required,

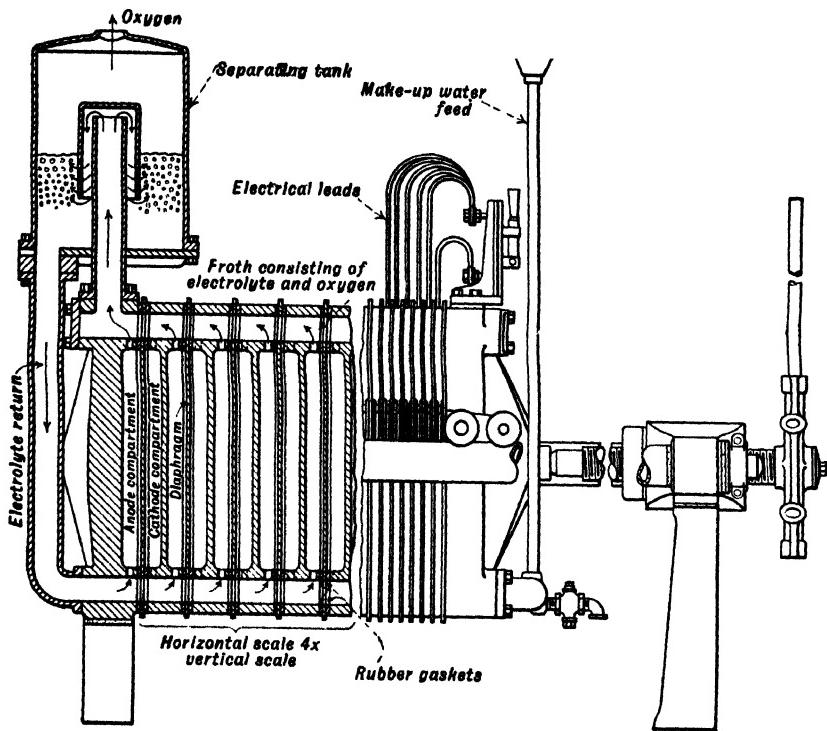


FIG. 144. Structural arrangement of Shriver electrolyzer.

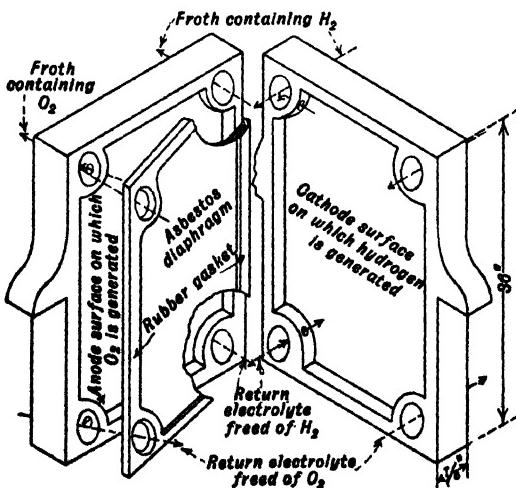


FIG. 145. Structural arrangement of Shriver electrodes and diaphragm.

an air-cooled condenser and gas-scrubbing tanks are supplied, but this is not ordinarily necessary.

The cell with electrode plates 3 ft. square takes 300 amp.; the 60 cells require 120 volts, or 2 volts per cell. The number of cells can be increased or lessened to meet the voltage available. Four or five 300-amp. knife switches are mounted above the electrolyzer so connected in the circuit that end cells may be cut off or added as desired. This arrangement is convenient when two or more electrolyzers are connected in parallel and it is necessary to balance the voltage.

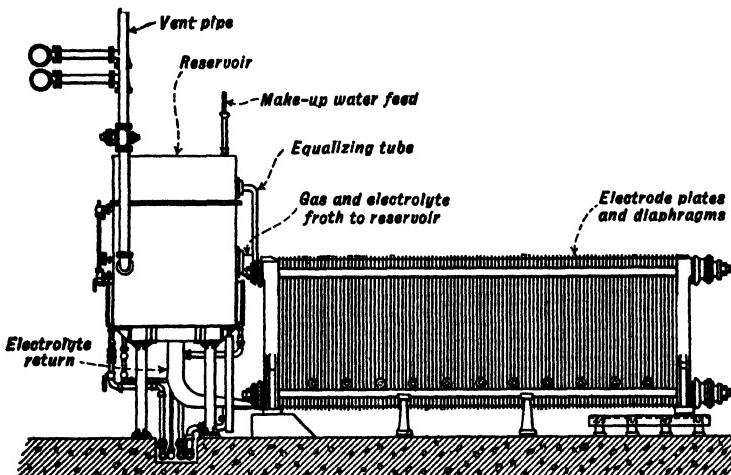


FIG. 146. Pechkranz filter-press type of hydrogen-oxygen generator.

The oxygen generated is 99.64 per cent pure or better; the hydrogen is 99.86 per cent pure. The generators have an output of 3.6 cu. ft. of oxygen and 7.2 cu. ft. of hydrogen per kw-hr. They are built in various sizes having capacities of 100 to 12,000 cu. ft. of oxygen and double the amount of hydrogen per 24 hr. The largest machine occupies a floor space of 6 by 26 ft.

Pechkranz Electrolyzer. The Pechkranz electrolyzer, like the Knowles cell, is of European origin, but a number of installations are located in the United States and Canada.⁴ It is a widely used oxyhydrogen generator in Europe.

The electrolyzer, shown in Fig. 146, is of the filter-press type. It consists essentially of a series of cells, each formed by two circular electrodes separated by a porous diaphragm cemented into a circular frame. The electrodes are bipolar, that is, one side is positive and the other

⁴ R. T. Elworthy, *Chem. & Met. Eng.*, 38, 714 (1931).

negative. The required number of electrodes and diaphragm frames are bolted up tightly between two cast-iron end plates which themselves constitute the end electrodes.

The electrodes are made of sheet iron, heavily nickel plated on the anode side. At the top are two holes coinciding with similar holes in the diaphragm frames as shown in Fig. 147. When the electrodes and diaphragms are pressed together, these holes form channels running the length of the electrolyzer, one carrying off hydrogen, the other oxygen, to their respective gas washers. Corresponding openings at the

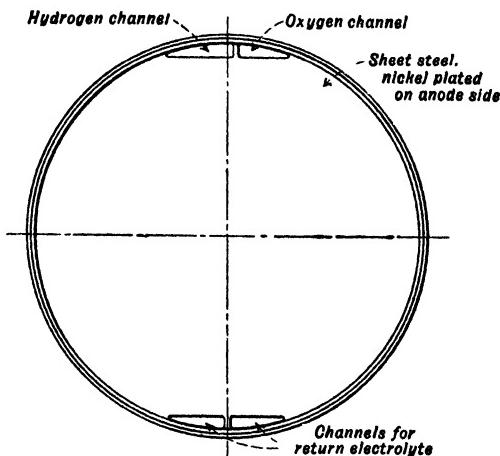


FIG. 147. Electrode, Pechkranz electrolyzer.

bottoms of the electrodes provide for the return circulation of the electrolyte. At one end of the unit are two reservoirs in which the oxygen and hydrogen are separated from the foam electrolyte. Here the gases are washed, distilled water is added to the electrolyte, and the electrolyte is cooled before recirculation.

The electrodes are about 6 ft. in diameter. An electrolyzer consisting of 110 cells is 25 ft. long and weighs about 30 tons.

A special feature of the Pechkranz electrolyzer is the employment of a metallic diaphragm, made of a sheet of pure nickel, perforated with exceedingly fine holes less than 0.004 in. in diameter. There are 5,000 to 6,000 perforations per square inch. The diaphragms do not deteriorate with use. Packing between the electrodes and the diaphragm frames is composed of plaited mineral fibers impregnated with a special unsaponifiable hydrocarbon. The upper part of the diaphragm is unperforated and forms a gas chamber; the next zone is perforated with exceedingly fine holes, followed by the main zone with larger perforations. The diaphragm is 0.004 in. thick and offers a negligible resistance to the passage

of the current. The nickel itself takes no part in the passage of the current, which is conducted solely through the liquid filling the perforations. These perforations are square to prevent gas bubbles from covering them. The diaphragm is reinforced by nickel-plated iron cross-bars riveted to the plate by nickel rivets. At the top and bottom are openings for gas and electrolyte channels to correspond with those in the electrode plates as shown in Fig. 148.

The two reservoirs placed at one end of each cell are made of welded steel plate, and each consists of three sections: the gas separator,

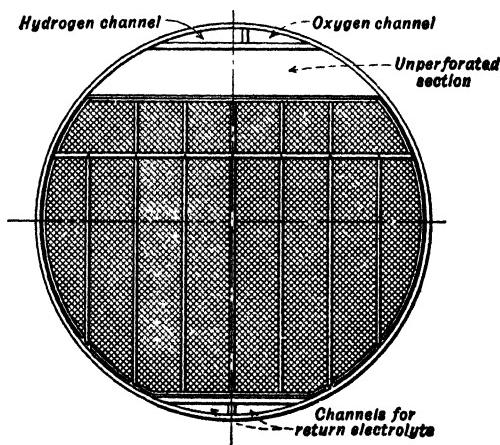


FIG. 148. Perforated nickel diaphragm, Pechkranz electrolyzer.

washer, and electrolyte cooler. Each reservoir is 6 ft. high, 5 ft. wide, and 4 ft. in breadth, and stands 5 ft. above the ground level. The foam of electrolyte and gas passes from the collecting pipes into the middle section, where the gas separates and bubbles up through distilled water in the top section. The electrolyte then runs into the lower section where it is cooled by contact with pipes through which cooling water is circulated. The electrolyte then passes back to the cells. The distilled water drops into the electrolyte, and the washed gases pass out through pipes. The warm water from the cooler is made available for heating the building or for supplying the distilled-water apparatus. The make-up water is a constant stream of distilled water flowing into the washer. The maximum distilled-water consumption is 7.5 gal. per 1,000 cu. ft. of hydrogen and frequently approximates the theoretical consumption of 5.0 gal.

The electrolyte consists of a 25 per cent potassium hydroxide solution. The purity of the hydrogen is 99.5 to 99.9 per cent; that of the oxygen, 98.5 to 99 per cent. The electrolyzer is operated at 80° C. (176° F.). The e.m.f. required is 2 to 2.5 volts per cell, and up to

150 cells can be built up in one electrolyzer. Two units in series take 700 volts and up to 2,000 amp. For small installations motor-generators are commonly used; mercury-arc rectifiers have proved satisfactory where large blocks of power are available and a number of electrolyzers are installed.

Pressure Electrolyzers. The Noeggerath Cell. In the cells thus far discussed, the gases liberated are under pressures but slightly greater than atmospheric. If the gases are to be transported in containers,

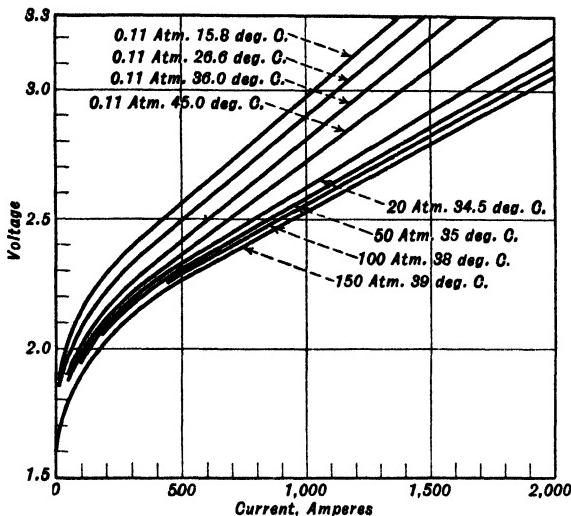


FIG. 149. Voltage-current relations in hydrogen-oxygen cells at various temperatures and pressures.

compressors are necessary for compressing them. If the confining spaces for the gases produced by the electrolyzer are limited, the pressure will gradually rise as the gases are generated. By proper construction of cells, gases can be generated at pressures of 200 atmospheres or nearly 3,000 lb.

Pressure electrolysis offers a saving not only in the investment and operation of compressors, for the voltage required for decomposition of water at higher pressures is lower than at atmospheric pressure, as shown in Fig. 149. This reduction in energy consumption at high pressures at first thought seems anomalous. The electrolysis at higher pressures would require a higher voltage if other factors remained the same, but the surface tension of the minute gas bubbles formed at the electrodes is so great that a 200-atmosphere pressure in the generator becomes insignificant in comparison, so that increased energy required at high pressures is slight compared to that at atmospheric. As shown

in Fig. 136, the volume of the gas bubbles in the electrolyte affects the electrical resistance. At the high pressures these bubbles are compressed so that the resistance is lowered. Similarly, the polarization due to the bubbles adhering to the electrodes is reduced as the pressure rises. These factors working to reduce the electrode voltage in pressure electrolyzers outweigh the opposite factors, so that the net voltage decreases as the pressure rises.

The construction of single-cell pressure electrolyzers for producing pure gases is comparatively simple if low voltages are to be used, but

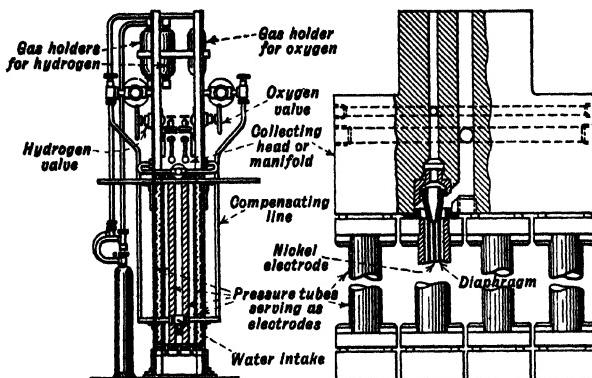


FIG. 150. Noeggerath cell for producing hydrogen and oxygen at 150 atmospheres pressure.

for operation at commercial voltages, cells should be connected in series, and this introduces difficulties due to leakage. Furthermore, if the oxygen and hydrogen are not removed uniformly, equal pressures will not be maintained on opposite sides of the diaphragm. Unequal pressures will cause mixing of the gases and may injure the diaphragm. At 200 atmospheres, for example, a difference in pressure of only 1 per cent will result in a net pressure of approximately 30 lb. per sq. in. on the fragile diaphragm.

The Noeggerath electrolyzer producing gases at 150 atmospheres pressure is pictured in Fig. 150. Four pressure tubes are shown, which constitute the pressure cells and which also serve as electrodes. Running along the axis of each tube is a nickel electrode, and surrounding this concentrically is the diaphragm. The gases pass upward into the collecting head through check valves and up to the gas holders; from there they are conducted to cylinders.

In operation, the cells are subjected to a definite voltage. The current increases as the pressure rises. When the desired pressure of

150 atmospheres has been obtained, the valves to the cylinders are closed, the cylinders are removed, and empty ones are connected. When the valves to the cylinders are opened the pressure drops to a value corresponding to the volume.

The electrolyte used is potassium hydroxide. The yield is approximately 10 cu. ft. of hydrogen per kw-hr. The guaranteed purity of the gases is 98 per cent, but 99.1 per cent oxygen and 99.8 per cent hydrogen have been obtained.

Packaging and Transportation of Gases. When the gases are to be shipped any appreciable distances they are compressed under high pressure and put in cylinders. In a large number of installations, however, the gases are manufactured at the plant where they are used. This is true, for instance, in large steel plants where oxygen and hydrogen are used for welding or cutting, and in plants for hydrogenation of oils. The gases are compressed to some convenient pressure, as 300 lb., for piping to the point of use, where by means of regulating and reducing values the pressure is reduced to the desired value. In other plants the gases are placed in portable drums at some intermediate pressure and are taken to the job at points not reached by the piping systems.

CHAPTER XIII

CORROSION

Corrosion of metals is a very important form of waste; not only is the replacement cost involved but also the rapid depletion of our ore supply is affected by corrosion. A good share of the corroded metal is recovered as scrap, but a large tonnage must be replaced by new metal.

The ferrous metals figure very prominently in corrosion problems, for they make up the greatest tonnage of our engineering metals and are readily subject to corrosion. In order to reduce corrosion it is desirable not only to understand the important factors that affect corrosion but also to have a working theory as to its mechanism. A number of theories have been proposed, each of which explains some phenomenon more satisfactorily than the others. That of widest applicability and widest acceptance at present is the electrochemical theory of corrosion.

Electrochemical Theory of Corrosion. The electrochemical theory of corrosion was developed by Whitney.¹ As new information became available, others, notable among whom are Walker² and his associates and Cushman,³ contributed to the theory.

The theory is based on the Nernst theory of electrolytic solution pressure which is briefly considered on page 29 and is discussed more fully by Creighton in Vol. I. Every metal has a tendency to go into solution with the formation of ions. This tendency initiates and helps to maintain corrosion. Referring to the electromotive series, Table VII, page 38, the metals listed at the top of the table, i.e., the more electronegative ones, have a marked tendency to go into solution. This tendency, the electrolytic solution pressure, decreases progressively down the list.

Applying the theory especially to ferrous metals, a large number of local couples, consisting of anodes and cathodes, cover the surface of the

¹ W. R. Whitney, *J. Am. Chem. Soc.*, **25**, 394-406 (1903).

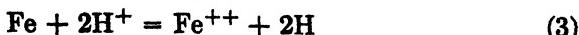
² W. H. Walker, Anna M. Cederholm, and L. N. Bent, *ibid.*, **29**, 1251-1264 (1907); and W. H. Walker, *Trans. Am. Electrochem. Soc.*, **14**, 175-187 (1908).

³ A. S. Cushman, *U. S. Dept. Agr. Bull.*, **30**, Office of Public Roads (1907); *Proc. Am. Soc. Testing Materials*, **7**, 211 (1907).

metal and current flows between them.⁴ There may also be neutral areas. The following reactions can be considered as taking place,



These two equations can be added to give



The metal corrodes wherever reaction 1 takes place; it is protected wherever reaction 2 takes place. It should be remembered that these are the electrode reactions of a voltaic couple and neither can take place alone. Any condition that retards reaction 2 also retards reaction 1, and corrosion is checked. Moisture must be present either to supply or to carry the hydrogen ions; iron will not corrode at normal temperatures in the complete absence of moisture.

For the corrosion represented by equation 1 to proceed it is necessary for the liberated hydrogen, equation 2, to be removed, for it produces a polarizing film and thereby arrests further action. The hydrogen may be removed by several processes. In one, oxygen dissolved in the water oxidizes the atomic hydrogen to form water,



Under such conditions there is no visible evolution of hydrogen. Ferric salts, if present, may likewise aid in removing the hydrogen. In another process two atoms of hydrogen combine to form gaseous molecular hydrogen, which can escape as bubbles:



If the hydrogen ions are present in high concentration the deposition of atomic hydrogen, equation 2, is relatively easy; therefore the tendency for iron to corrode is increased by a high hydrogen-ion concentration, i.e., by an acid solution.

On the other hand, as the concentration of ferrous ions in the solution increases as the result of reaction 1, the effective solution potential of the iron decreases and corrosion slows down. According to the Nernst equation, a tenfold increase in the concentration of monovalent metal ions in solution decreases the metal potential 0.058 volt at room temperature. For bi- and trivalent ions the change is one-half and one-third as great, respectively.

When the liberated hydrogen is oxidized to form water, a film of electrically neutral hydrogen atoms is built up on the cathodic surface of the metal. This film polarizes the metal and thus interferes with the progress of corrosion by retarding the further solution of iron. An active

⁴ R. Landau, *Trans. Electrochem. Soc.*, 81, 363 (1942).

oxidizing agent, such as dissolved oxygen or dissolved ferric salts, acts as a depolarizer by combining with the atomic hydrogen; this permits more hydrogen to plate out and consequently more iron to go into solution.

When hydrogen is being evolved as a gas, the overvoltage of hydrogen on the cathodic surface is an important factor affecting the rate of corrosion. In natural waters the overvoltage on iron is usually sufficiently high to prevent gas evolution.

Practically always the reaction represented by equation 3 is considerably more rapid than that of either 4 or 5, so that it is the velocity of the latter two reactions, either singly or jointly, that determines the rate of corrosion, for as previously mentioned the iron can go into solution no faster than hydrogen plates out, equation 3, but this reaction can take place no faster than the removal of hydrogen, equations 4 or 5. Walker⁶ and Speller⁸ found that in natural water the rate of corrosion is proportional to the oxygen content, with the conclusion that reaction 4 is the controlling one. In neutral or alkaline solutions, reaction 5 is very slow so that reaction 4 controls the corrosion rate; but in strongly acid solutions reaction 5 usually predominates. In a narrow acid range both reactions are nearly of the same rate, and, therefore, both affect the rate of corrosion.

A reaction that might appear to affect the rate of corrosion is the conversion of ferrous iron to the less-soluble ferric iron. When iron goes into solution as indicated in equation 3 it does so in the ferrous form. Oxidizing conditions will change the iron to the less-soluble ferric form, and thus by removing iron from the solution will tend to accelerate further corrosion. This, however, is of little importance as affecting the rate of corrosion, for the rate of reaction can be considerably reduced and still be faster than 4 or 5. In other words, the rate of corrosion is affected largely by factors affecting reactions 4 and 5 rather than reaction 3.

Although the above discussion is based on the corrosion of ferrous metals, the theory applies to non-ferrous metals as well. Watts,⁷ however, points out a number of cases in which corrosion is apparently non-electrolytic.⁸

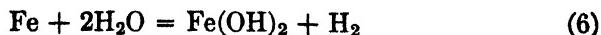
⁶ W. H. Walker, *loc. cit.*

⁸ F. N. Speller, *J. Franklin Inst.*, **193**, 523 (1922).

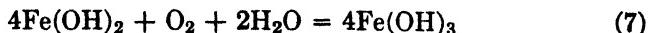
⁷ O. P. Watts, *Trans. Electrochem. Soc.*, **67** (1935).

⁸ For a more complete discussion of the electrochemical theory of corrosion, the reader is referred to F. N. Speller, *Corrosion, Causes and Prevention*, McGraw-Hill Book Company, 1935; W. D. Bancroft, "The Electrolytic Theory of Corrosion," *J. Phys. Chem.*, **28**, 785-871 (1924); A. A. Pollitt, *The Cause and Prevention of Corrosion*, D. Van Nostrand Company, New York, 1924; and U. R. Evans, *Metallic Corrosion, Passivity and Protection*, Arnold, London, 1937.

The Role of Oxygen in Corrosion. In the preceding section mention was made of the fact that oxygen may promote corrosion by removing the hydrogen from the cathodic surface according to equation 4. It also aids in removing iron from solution as mentioned, for when the anodic surface goes into solution it does so as ferrous iron:



and oxygen converts this to the less-soluble ferric form:



The rust film formed becomes cathodic to an unruled metal surface; i.e., the rusted surface becomes ennobled. The clean surface becomes anodic and goes into solution. Aston⁹ showed that wet rust acts as a diaphragm protecting the underlying metal from direct access of oxygen, thereby checking corrosion. When two pieces of iron are placed in the same solution and one is exposed to the action of dissolved oxygen and the other is protected from the oxygen by wet rust, the shielded iron becomes anodic to the other one. This is true not only of ferrous metals but also of a number of other metals as shown by Evans.¹⁰

In connection with the corrosion of steel, Evans¹¹ calls attention to the fact that a drop of brine placed on a steel plate causes corrosion below its center, but near the edge of the drop, where oxygen has access to the metal, there is no attack at all. Likewise, a vertical steel sheet, partly immersed in brine, corrodes at the lower part; the aerated (cathodic) zone immediately below the water level remains uncorroded for a considerable time. This is because near the surface the oxygen produces a thin oxide film and diverts corrosion to the lower part where there is little oxygen. If this oxide film existed over the whole surface of the metal it would probably be incapable of protecting the metal. It will readily be seen that there must be some corrosion at the protected aerated parts of the metal in order to produce an oxide film.

Oxygen, therefore, may play a double role in corrosion: (1) It promotes corrosion by removing atomic hydrogen, equation 4, but the corrosion is not promoted at the point of access of the oxygen (cathodic surface) but at the anodic surface at another point. (2) It forms an oxide film which lowers the oxygen concentration beneath it; this leaves the areas of higher oxygen concentration cathodic to the screened portion and thus diverts the corrosion to some other point where oxygen

⁹ J. Aston, *Trans. Am. Electrochem. Soc.*, **29**, 449 (1916).

¹⁰ U. R. Evans, *J. Inst. Metals*, **30**, 239 (1923); *Trans. Faraday Soc.*, **18**, 1 (1922); **19**, 201 (1923); **18**, 789 (1924).

¹¹ U. R. Evans, *J. Soc. Chem. Ind.*, **45**, 504 (1926).

is not as readily accessible. Degassers have been developed for removing oxygen from boiler feedwaters; they are designed to remove the air or the oxygen only.

For a number of metals the primary corrosion product is a continuous and non-porous layer which protects the metal against further corrosion; or a protective film is formed in the presence of oxygen. Most such metals are alloys containing aluminum, cobalt, chromium, nickel, or silicon. Surface films containing one or more of these metals afford good protection against further corrosion, except under special conditions, as in the presence of chlorides.

The deterioration of reinforced concrete by salt, brine, and sea water has been studied by Creighton.¹²

Protective Metallic Coatings. In many cases corrosion is due to the formation of a galvanic couple, particularly when two dissimilar metals are in contact with each other and both are exposed to a solution that serves as an electrolyte. It is not necessary that the electrolyte be a solution of even moderate concentration; rain water will contain enough carbon dioxide and salts washed from the atmosphere to serve as an electrolyte to promote galvanic action. All natural waters act likewise, and if the metal surface has been touched by human hands, salts from the surface of the skin aid in making the water more conducting.

Referring to the electromotive series, Table VII, page 38, when two of the metals form a galvanic couple the electronegative one¹³ is anodic and tends to go into solution while hydrogen tends to plate out on the more-electropositive metal. The latter metal may, therefore, be protected from corrosion at the expense of the former.

A protecting or decorative coating of one metal over another may protect the base metal or it may accelerate its corrosion, depending upon whether it is electronegative or electropositive to that metal, provided that the base metal is not entirely covered. It is an unfortunate fact that metal coatings, whether applied by electrodeposition or by hot dipping, may easily contain "pin holes" in which the base metal is exposed. In the presence of moisture a voltaic couple is produced; the more-electronegative metal will corrode and the other metal will be protected.

¹² H. J. Creighton, *J. Franklin Inst.*, 184, 689 (1917).

¹³ In the discussion of the electromotive series, Chapter II, attention was called to the confusion that has existed in regard to the sign of the potentials and to the fact that now, with the exception of the *International Critical Tables*, zinc is internationally called negative. To add to the confusion, many current writers, who otherwise adopt the potentials with the zinc negative, still call zinc electropositive to iron, and similarly with other metal combinations. In this book zinc is called electronegative or anodic to iron, iron electropositive or cathodic to zinc.

The classical examples usually cited are zinc and tin used as protective coats on iron; both zinc and tin plate may contain pin holes when applied as protective coatings. Zinc is anodic to the iron and goes into solution and thus protects the iron. Eventually the iron will be exposed in areas sufficiently large that zinc can no longer protect it. The effective protecting distance is generally a fraction of an inch in fairly pure water, but in sea water it may amount to more than a foot. In tin coverings, however, the more-electronegative iron goes into solution and protects the tin. This is true in many cases, but tin plate has many useful applications where the surface is not allowed to remain wet for any length of time.

If an impervious coating of metal is obtained the more-electropositive coating will as a general rule give better corrosion resistance because its electrolytic solution pressure is less. If the coating metal is ductile, burnishing operations subsequent to the deposition may flow the metal sufficiently to close any pores and thus give excellent protection to a more-electronegative metal, for there is no opportunity for galvanic corrosion, except that subsequent wear or injury to the coat may expose the base metal. Thus, lead, copper, silver, and gold may be burnished to produce an impervious coating.

Galvanic corrosion may be checked by its own action if the products of corrosion themselves form an impermeable protective coating. In dairy equipment, a thin film of oil (butterfat) on the surface prevents electrolytic action.

Galvanic corrosion is the cause of much localized corrosion. Thus, mill scale on the surface of iron is electropositive (cathodic) to the iron. In contact with an electrolyte such as ground water, the metal may fail because of pitting caused by galvanic corrosion before more than 10 to 20 per cent of its weight has been corroded away. It has been found that, if two similar pieces of pipe are taken, one coated with mill scale and the other with the mill scale removed, the latter will corrode much less than the other. In wrought iron the irregular distribution of the slag produces conditions conducive to localized corrosion. In fact, it was once assumed that lack of homogeneity in a metal was essential to corrosion and that a fairly pure metal would corrode but slightly; investigations, however, indicate that it is only a minor factor in the *amount* of corrosion, but may under certain conditions be an important factor in determining the nature and the distribution of corrosion. Watts¹⁴ has shown that in some cases no galvanic corrosion will take place if oxygen is excluded.

¹⁴ O. P. Watts, *Trans. Electrochem. Soc.*, 57, 235 (1935).

Pin-Hole Tests. Various methods have been devised to test metal coatings for pin holes. In the Walker test a weak solution of potassium ferricyanide, $K_3Fe(CN)_6$, and a small amount of sodium chloride in gelatin is applied warm to a piece of plated iron. Blue spots of Prussian blue, $Fe_4[Fe(CN)_6]_3$, appear where iron is exposed. Agar-agar also suggested by Walker appears to be more satisfactory than gelatin. Such a solution may consist of

	GRAMS
Sodium chloride, NaCl	60
Potassium ferricyanide, $K_3Fe(CN)_6$	6
Agar-agar	30
Alcohol, C_2H_5OH	250
Water to 1 liter	

In the Burns test, applicable for coatings of nickel, chromium, and tin or steel, the plated object is immersed in a dilute salt solution containing a trace of hydrogen peroxide. Spots of bright red iron rust appear wherever the steel is exposed.

The above tests fail when applied to zinc coatings on iron and steel, for the zinc is anodic to the iron and consequently no iron ions are formed in the local couple when the test solution is applied, and no coloration is produced.

The process of reversing the electrolysis has been studied by Koehler and Burford.¹⁵ By applying an external e.m.f. the blue coloration can be produced with the ferricyanide solution wherever iron is exposed beneath the zinc plate. Two or more dry cells are connected in series; the positive terminal is connected to the test plate by piercing the gelatin or agar-agar solution if necessary; the negative terminal contacts the solutions only. Likewise, test papers, impregnated with potassium ferricyanide and placed moist over the metal-coated plate, will give a blue coloration, with an external e.m.f. applied if necessary. These checks have been applied successfully for field testing of zinc-coated road culverts.

Electrolytic Protection against Corrosion. When metals corrode, local couples are formed on the surface, some parts serving as anodes and therefore corroding, other parts serving as cathodes and thus being protected. If the whole surface is made cathodic to a separate anode and sufficient voltage is available between the two electrodes, corrosion can be checked over the whole surface. In order to obtain cathodic protection at least a minimum amount of current must flow from the anode to the cathode.

¹⁵ W. A. Koehler and R. O. Burford, *ibid.*, 70, 397 (1937).

Cathodic protection has been applied to many types of structures, and development has been rapid in recent years. It is applied to prevent or check corrosion in boilers, condensers, underground oil and water pipes, water tanks, and a variety of other kinds of industrial equipment.¹⁶

Cathodic protection can be achieved by two methods, the protective action being brought about by the same process in both. (1) A potential is generated by means of some metal or alloy which has a greater solution pressure than the one it is intended to protect. The two metals form a voltaic couple; the anode goes into solution and must be replaced from time to time; the cathode is protected against corrosion. This process is used widely in the protection of non-ferrous structures. (2) A voltage from an external source is applied to an anode, the surface to be protected serving as cathode. Means for supplying direct current must be available. This method is used largely in the cathodic protection of ferrous structures.

The first method was formerly applied for the prevention of corrosion in steam boilers, condenser tubes, and economizer tubes. At first it was considered necessary to use zinc for anodes, but later it was found that steel gave satisfactory results. In fact, when zinc is used there is danger of reversal of polarity between the zinc slabs and the iron of the boiler, for after a time the zinc becomes covered with a deposit either of its own corrosion or products of scale-forming matter from the water, and this material, instead of being anodic to the iron, is cathodic and may actually stimulate corrosion of the boiler. The steel or zinc protector blocks are placed in the water-ends, electrically connected with the tube plate or condenser body, forming an electric couple with the tubes to be protected. The blocks are placed opposite and parallel to the tube plate and may be replaced when they become worn. The protection afforded by such blocks does not extend far into the tubes, usually less than 18 in. Alloy blocks consisting largely of aluminum have been found to give fairly good results, but on the whole the method did not prove satisfactory.

Zinc plates are used on practically all sea-going ships to protect the steel hull near the propellers. With bronze propellers, a steel hull, and sea water, an excellent voltaic couple is formed, the more-electro-negative steel serving as anode and, therefore, corroding rapidly. With zinc blocks bolted to the hull, both the steel and bronze are cathodic to the zinc and are protected. On a 200-ft. ship, about which the author has information, three zinc blocks about 4 by 8 by 1 in. are placed on the hull and propeller struts at points nearest the propeller.

¹⁶ R. H. Brown and R. B. Mears, *ibid.*, 81, 455 (1942), in an article entitled "Cathodic Protection," give a large number of references on the subject.

The second method is being applied to boilers, condensers, oil and water pipes, and water tanks. For underground and underwater pipes the protection is applied to the outer surface of the pipes; for water tanks it is applied to the inner surfaces. Hundreds of miles of oil and water pipe and hundreds of water tanks are protected cathodically.¹⁷ For oil and water pipes carbon anodes are commonly used. For water tanks, one or more electrodes, usually of stainless steel or graphite, are sus-

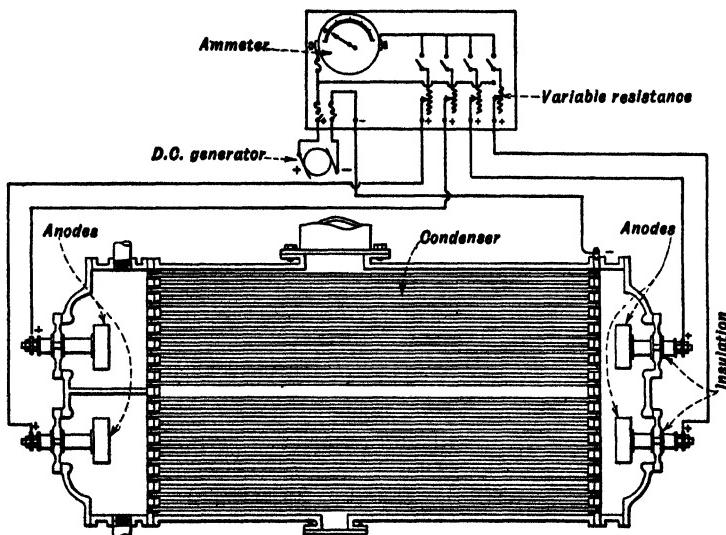


FIG. 151. Cumberland installation in a surface condenser.

pended from the roof of the tank into the water. For a 350,000-gal. tank Norman gives the annual cost of cathodic protection as \$60 for the fixed charges and \$12 for the electric service, a total of \$72 against an annual cost of \$190 for painting. Bardwell¹⁸ states that for a certain tank an amperage of 3 amp. is required per 10,000 sq. ft. of surface to be protected; the voltage required is 10 volts. An ordinary 110-volt lighting circuit is used through a cabinet which contains a transformer and rectifier. Copper oxide rectifiers are commonly used for this purpose.

Cumberland,¹⁹ a pioneer in the development of cathodic protection, applied the method to boilers and condensers. Current densities of 0.001

¹⁷ E. E. Norman, *J. Am. Water Works Assoc.*, **32**, 1069 (1940); W. C. Mabee, *ibid.*, p. 1075; T. H. Wiggin, *ibid.*, p. 1077.

¹⁸ R. C. Bardwell, *Trans. Am. Inst. Chem. Engrs.*, **37**, 923 (1941).

¹⁹ E. Cumberland, *J. Inst. Metals*, **15**, 192 (1916), and *Trans. Faraday Soc.*, **11**, 277 (1915).

to 0.005 amp. per sq. ft. of cathode surface are sufficient. Anodes are pieces of cast iron or steel submerged in the water and insulated from the rest of the boiler or condenser. An e.m.f. of 10 volts is ordinarily sufficient. Figure 151 shows an application of the Cumberland method to a surface condenser.

Some investigators feel that electrolytic protection has been over-emphasized and that sometimes it may do more harm than good. It must be remembered that parts remote from the anodes may not be sufficiently protected, and the danger is mainly in a feeling that the corrosion problem has been fully solved when it may not be in actuality.

Stray-Current Electrolysis. In most electric railway systems, particularly in cities, the power is supplied as direct current commonly at

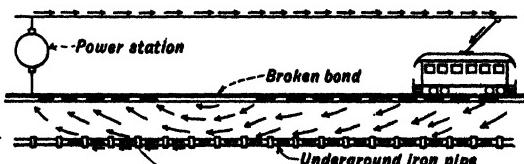


FIG. 152. Illustrating stray-current electrolysis.

600 volts. The current passes along an overhead trolley wire, through the motor and control system of the car, and back along the rails. As a rule, the rails are not insulated from the ground, especially not in wet weather. The ground, therefore, supplies a parallel circuit for the current; and although the resistance of the ground circuit is high, some current will flow through it. Conduction through the soil is ionic through the water solution in its pores.

The chief objection to earth conduction is that in cities there are many lines of pipe and cable running parallel with the railway tracks. Such lines furnish a conducting medium that is superior to the earth, and the tendency is for the ground current to be diverted to them as shown in Fig. 152. Where the current enters the pipe, the pipe is cathodic and suffers no corrosion; but where the current leaves the pipe, the pipe is anodic and corrosion is severe. One ampere-year at 100 per cent current efficiency will dissolve 20.1 lb. of ferrous iron or 74.5 lb. of lead. To this must be added natural corrosion due to salts in the soil. Figure 153 shows corrosion of lead cable sheaths by stray-current electrolysis.

A number of methods have been proposed for mitigating stray-current corrosion. One of the first essentials is the use of heavy rails properly bonded so as to reduce their resistance as a return circuit. A roadbed of high electrical resistance is an important aid. As a founda-

tion under the ties, clean crushed rock offers a much greater resistance than solid concrete. The use of copper conductors in parallel with the track may be of considerable help, but the copper costs may be excessive, and if the conductors are buried, the increased contact with the earth may augment stray currents. Insulated negative feeders to the tracks are very helpful in decreasing stray currents, but their cost is



FIG. 153. Lead cable sheaths damaged by electrolysis. (*Courtesy The Milwaukee Electric Railway and Light Company.*)

high and they cause power loss and voltage drop at the motors. The feeders should be connected to the tracks at more than one point. Another method is the "pipe drainage system" in which the pipes are made as good conductors as possible. This makes the pipe an integral part of the electric circuit and eliminates the chance of electrolytic conduction, except that, if for any reason the bond is broken, electrolytic corrosion will be very severe. At various points the pipe is connected to the rail or to the negative bus-bar through metallic conductors, as shown in Fig. 154. Stray currents can be avoided entirely by the use of the double trolley or the insulated third and fourth rails. The chief objection to the double trolley or underground system is the high cost. Alternating currents of commercial frequencies of 15 to 60 cycles per second cause no appreciable electrolytic corrosion. As shown by

McCollum and Ahlborn,²⁰ the corrosion is practically negligible with current reversals of 5-minute periods or faster. Alternating or reversed current with as long periods as a day or a week materially reduce the damage to underground structures. It appears that a reversal of current actually causes metal to be redeposited on the corroded portions. The redeposited metal may have little effect in strengthening the pipe



FIG. 154. Bond wires soldered to cable sheaths for drainage of stray currents.
(Courtesy The Milwaukee Electric Railway and Light Company.)

mechanically, but it will act as anode after reversal of current and thus protect the uncorroded metal beneath. The shifting of loads on electric systems in cities usually produces large areas called neutral zones, where the polarity of underground pipes reverses several times a day. This reversal checks underground corrosion considerably.

Other methods are also available for preventing stray currents or damage caused by them,²¹ but at the present time there is no general

²⁰ E. McCollum and G. H. Ahlborn, "Influence of Frequency of Alternating or Infrequently Reversed Current on Electrolytic Corrosion," *Natl. Bur. Standards Tech. Paper* 72, 1916.

²¹ E. B. Rosa and B. McCollum, "Electrolysis and Its Mitigation," *Natl. Bur. Standards Tech. Paper* 52, 1915.

tion under the ties, clean crushed rock offers a much greater resistance than solid concrete. The use of copper conductors in parallel with the track may be of considerable help, but the copper costs may be excessive, and if the conductors are buried, the increased contact with the earth may augment stray currents. Insulated negative feeders to the tracks are very helpful in decreasing stray currents, but their cost is

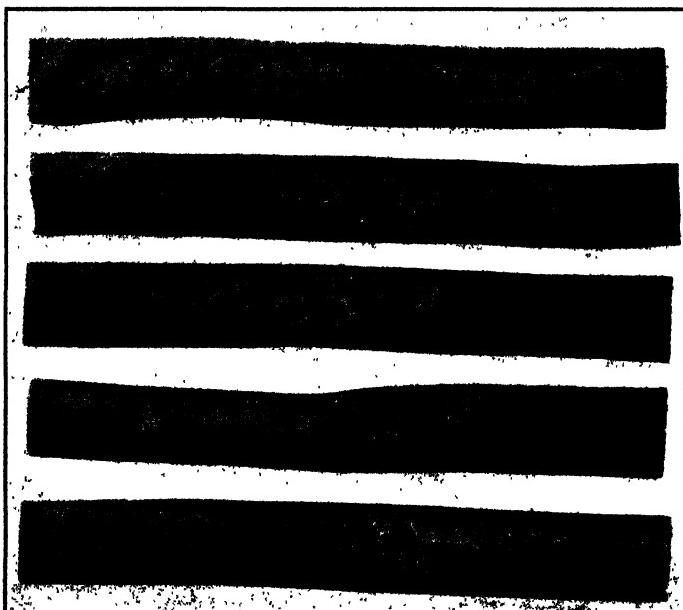


FIG. 153. Lead cable sheaths damaged by electrolysis. (*Courtesy The Milwaukee Electric Railway and Light Company.*)

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FIG. 154. Bond wires soldered to cable sheaths for drainage of stray currents.
(Courtesy *The Milwaukee Electric Railway and Light Company*.)

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²¹ E. B. Rosa and B. McCollum, "Electrolysis and Its Mitigation," *Natl. Bur. Standards Tech. Paper 52*, 1915.

agreement that one is much better than the others. Both the pipe drainage system and the insulated feeder system are widely used.

Steel reinforcing in concrete structures may also be subject to stray-current electrolysis.²² The current may be that of an electric railway system or that generated within a concrete building. Where the current leaves the steel, anodic corrosion occurs, with the liberation of oxygen or in some cases of chlorine; an iron oxide or a salt will be formed, and these chemical changes are accompanied by an increase in volume. When iron is changed to ferric oxide the volume is increased in the ratio of 1 to 2.2, and similar volume increases occur when other anodic products are formed. The increase in volume sets up forces sufficient to break concrete. Serious injury has resulted to concrete buildings from electrolysis of the reinforcing bars.²³ Coating the bars with a waterproof paint is helpful as long as the coating remains intact.

In locating the cause for stray-current electrolysis and in devising means for its mitigation, an electrolysis survey is very desirable. Methods for making such surveys have been described by McCollum and Ahlborn.²⁴

²² C. E. Magnusson and G. H. Smith, *Trans. Am. Inst. Elec. Engrs.*, **30**, 2055 (1911).

²³ H. P. Brown, *Eng. News*, **65**, 684 (1911).

²⁴ B. McCollum and G. H. Ahlborn, "Methods of Making Electrolysis Surveys," *Natl. Bur. Standards Tech. Paper* **28**, 1916.

CHAPTER XIV

ELECTROANALYSIS

It is not the object to discuss electrochemical analysis in this chapter so that it may be used as a laboratory guide, nor is it intended to treat in any detail the fundamental theory involved. Much of the theory is discussed in Vol. I; for laboratory detail, textbooks on analytical chemistry should be consulted.¹ This chapter merely gives a brief review of some of the commoner methods available.

Hydrogen-Ion Determinations. When an acid is dissolved in water, dissociation takes place:



and when the solution is sufficiently dilute the reaction will go completely to the right; i.e., the acid is completely ionized. Therefore, at this dilution, called infinite dilution, the H^+ ion normality is equal to the acid normality, but at greater acid concentrations the H^+ ion concentration is less than the concentration of the acid, both expressed in terms of normality. Table XXVII shows the relation between the

TABLE XXVII
RELATION BETWEEN NORMALITY AND HYDROGEN-ION CONCENTRATION
(Observations in distilled water at normal temperatures)

Acid	Equivalents of Hydrogen Ions per Liter	
	5 N acid	2 N acid
HNO_3	2.08	1.48
HCl	2.01	1.39
H_2SO_4	1.84	1.01
H_3PO_4	0.816	0.36
HAc	0.018	0.006

¹ H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*, 2 vols., Chemical Publishing Company, New York, 1940; Wm. Rieman, III, J. D. Nease, and B. Naiman, *Quantitative Analysis*, McGraw-Hill Book Company, New York, 1942; A. Fischer and A. Schleicher, *Elektroanalytische Schnellmethoden*, second edition, F. Enke, Stuttgart, Germany, 1926; A. Classen and H. Damsoo, *Quantitative Analyses durch Elektrolyse*, seventh edition, Verlag Julius Springer, Berlin, 1927.

normalities of several acids and the normalities of their H⁺ ions at certain concentrations.²

A knowledge of the H⁺ ion concentration is generally of more importance than that of the acid concentration, for very often rate of corrosion, rate of flocculation of precipitates, and conductivities of solutions are determined by the H⁺ ion concentration and not by the total acid concentration.³ In dilute solutions the H⁺ ion concentration can be determined with much greater accuracy than can the acidity by the usual titration methods.

For various purposes it has been found more practicable to express the normality of the H⁺ ion concentration not as such but as the negative logarithm to the base 10. This terminology was proposed by Sorenson in 1909 and has been generally accepted. He calls the number the *hydrogen-ion exponent* and designates it by the symbol pH. Accordinging to that,

$$\text{pH} = -\log_{10} C_H = \log_{10} \frac{1}{C_H}$$

$$C_H = 10^{-\text{pH}}$$

where the C_H indicates the concentration of the H⁺ ions.

In 0.01 N HCl, C_H = 0.01 = 10⁻², and pH = 2.

The H⁺ ion concentration is expressed as pH particularly in dealing with dilute solutions. Table XXVIII shows the relation between H⁺ ion normality and pH.

TABLE XXVIII
RELATION BETWEEN HYDROGEN-ION NORMALITY AND pH

Normality	Exponential	pH
1.0	10 ⁰	0
0.1	10 ⁻¹	1
0.01	10 ⁻²	2
0.001	10 ⁻³	3
0.000,1	10 ⁻⁴	4
0.000,01	10 ⁻⁵	5
0.000,001	10 ⁻⁶	6
.....
0.000,000,000,001	10 ⁻¹⁴	14

The electrometric H⁺ ion measurement is based on voltage measurements in two connected half-cells, one of the half-cells containing the

² F. N. Speller, *Corrosion, Causes and Prevention*, McGraw-Hill Book Company, New York, 1935.

³ The importance of H⁺ ion concentration in a variety of industrial processes is discussed in H. T. S. Britton, *Hydrogen Ions*, D. Van Nostrand Company, New York, 1932.

solution of unknown H^+ ion concentration and a suitable electrode, the other half-cell being one of a number of standard half-cells available.

The Hydrogen Electrode. Figure 155⁴ shows a concentration chain consisting of a solution of known H^+ ion concentration, and the solution of unknown H^+ ion concentration, joined by a bridge of neutral salt solution which has no significant effect on either. In each solution is a hydrogen electrode that is kept saturated with gaseous hydrogen at atmospheric pressure. The two electrodes are connected to a potentiometer which measures their potential difference as voltage. If the

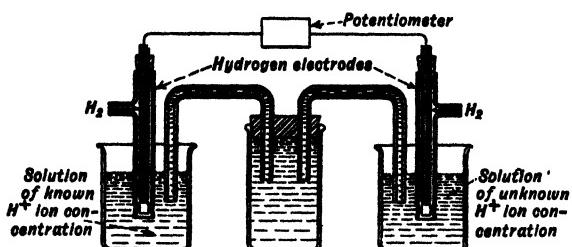


FIG. 155. Apparatus for determining hydrogen-ion concentration, using two hydrogen electrodes.

voltage is E , the known concentration C_n , and the unknown C_x , the relation of the voltage to the ratio of concentrations is:

$$\frac{E}{0.0001983T} = \log_{10} \frac{C_n}{C_x}$$

E = observed voltage
 T = temperature, °K.
 C_n = known H^+ ion concentration
 C_x = unknown H^+ ion concentration

If the temperature of the two solutions is 25° C., the equation becomes

$$\frac{E}{0.0591} = \log_{10} \frac{C_n}{C_x}$$

If the known solution is a normal H^+ ion solution ($pH = 0$), $C_n = 1$, and the electrode in it constitutes a theoretical normal hydrogen electrode. Since $\log_{10} \frac{1}{C_x} = pH$, the above equation can be written,

$$\frac{E}{0.0591} = pH$$

The Calomel Electrode. It is more practicable to use a calomel half-cell in place of the normal hydrogen electrode, for in the latter

⁴ Figures 155 and 156 are taken with slight modification from *Notes on Hydrogen Ion Measurements*, Note Book 3, Leeds and Northrup Company, Philadelphia, 1931.

case the solution of known H^+ ion concentration must be strongly buffered and its pH value must be accurately known and checked frequently. Figure 156 shows a more convenient arrangement for determining pH values. A calomel electrode replaces the hydrogen electrode and its solution of known H^+ ion concentration. The voltage reading will be higher, so that a subtraction must be made in order to apply the above equation. The values to be subtracted from the voltage reading are given in Table VI, page 35, for $25^\circ C$. For example, if a saturated calomel electrode is used, 0.2458 volt must be subtracted from the

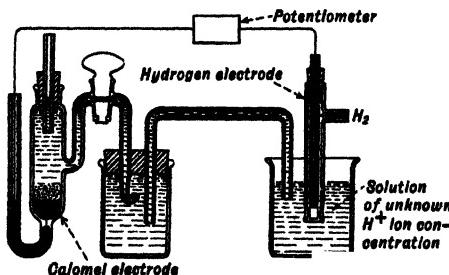


FIG. 156. Apparatus for determining hydrogen-ion concentration, using a hydrogen and a calomel electrode. This is a more practical method than that shown in Fig. 155.

voltage reading on the potentiometer in order to obtain E for the above equation.

The equation for a normal hydrogen electrode and a calomel electrode combination is

$$\frac{E - e}{0.0001983T} = \log_{10} \frac{1}{Cx} : pH$$

E = observed voltage
 e = calomel electrode potential
 T = temperature, °K.
 Cx = unknown H^+ ion concentration

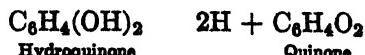
If a saturated calomel electrode is used, $e = 0.2458$; and if the system is at $25^\circ C.$, the equation becomes

$$pH = \frac{E - 0.2458}{0.0591}$$

The Quinhydrone Electrode. The quinhydrone electrode⁶ can be substituted for the hydrogen electrode in the solution of unknown H^+ ion concentration. It is very simple and convenient but is suited for use in only neutral or acid solutions. Quinhydrone is prepared by adding a ferric ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 \cdot 12H_2O$, solution

⁶ E. Billmann, Ann. chim., 15, 109 (1921); E. Billmann and H. Lund, Ann. chim., 16, 331 (1921); 19, 137 (1928).

(100 g. in 300 cc. water at 65° C.) to a solution of hydroquinone, para $C_6H_4(OH)_2$, (25 g. in 300 cc. water). The quinhydrone precipitates in fine needles and can be filtered off and washed. When dissolved in water it dissociates, giving a definite hydrogen partial pressure:



Therefore, a little of the quinone is added directly to the solution of unknown H^+ ion concentration. A platinum or gold electrode is immersed in the solution, the solution is connected with a suitable salt bridge to a calomel half-cell, and the voltage is read on a potentiometer.* If a decinormal calomel electrode is used, the pH can be calculated from the equation

$$pH = \frac{0.3665 - 0.00068(t - 18) - E}{0.0577 + 0.0002(t - 18)} \quad E = \text{voltage reading} \\ t = \text{temperature, } ^\circ\text{C.}$$

The Glass Electrode. If a glass membrane is placed between two liquids of differing H⁺ ion concentration, the concentration in one of the solutions may be calculated from potential measurements if the H⁺ ion concentration of the other solution is known. The glass must be of a special type, high in sodium and calcium content and low in aluminum and potassium. MacInnes and Dole⁷ recommend a glass having the composition SiO₂ 72, Na₂O 22, and CaO 6 per cent.

A common form of glass electrode is illustrated in Fig. 157. A thin glass bulb is blown at the end of a glass tube. A solution of hydrochloric acid 0.1 N or less is put in the tube, and a little hydroquinone is added to the acid. A platinum wire makes contact with the solution, and the tube is usually sealed. This combination produces a quinhydrone electrode. The glass electrode is immersed in the solution for which the hydrogen-ion concentration is desired. A calomel electrode is also inserted in the solution, and the voltage across the two electrodes is measured. The voltage is

$$E = E_G + 59.1 \log_{10} Cx - e$$

E = observed voltage
 E_G is determined empirically
 Cx = H^+ ion concentration of the unknown solution
 e = calomel electrode potential

⁴ For further discussion of the quinhydrone electrode see Vol. I, and also I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, second edition, John Wiley & Sons, New York, 1931; and I. M. Kolthoff, *The Colorimetric and Potentiometric Determination of pH*, John Wiley & Sons, New York, 1931.

¹D. A. MacInnes and M. Dole, *J. Am. Chem. Soc.*, **53**, 29 (1931).

The value of E_G is a function of the nature and concentration of the solution in the glass electrode and of the temperature of the system; it cannot be calculated from known data. To determine E_G the glass electrode and a hydrogen electrode are immersed in a suitable solution of hydrogen ions, e.g., 0.05 M hydrochloric acid; the hydrogen-ion concentration of the solution need not be known. The cell potential thus obtained is the value of E_G for that particular electrode.

The glass electrode is of more general application than either the hydrogen or conventional quinhydrone electrodes. It is applicable over

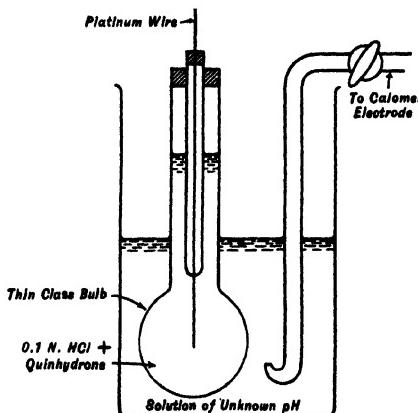


FIG. 157. A glass electrode.

a pH range of 0 to 9 or even higher. A variety of glass electrodes have been developed in the last few years.

Glass electrodes are now incorporated in portable pH meters, consisting of a glass electrode, saturated calomel electrode, a small glass beaker for the solution to be tested, a vacuum-tube potentiometer, and standard cell, all assembled in a compact case. The meter is graduated to read directly in pH units with a compensating device for temperature variations from 25° C. E_G is determined by putting a solution of known pH in the beaker, setting the potentiometer indicator to the pH for that solution, and then adjusting a compensating dial until the galvanometer reads zero. The instrument is then ready for determining the pH of the unknown solution which is placed in the small beaker.

Antimony Electrode. The antimony electrode consists of a piece of pure antimony used as an electrode in the solution; a calomel electrode commonly serves as the other electrode. The preparation and care of the antimony electrode are somewhat tedious, and so some of the refinements in connection with its use and care are not always carried out.

Its usefulness is based on its ruggedness rather than its accuracy. It has found considerable application for continuous pH measurement in industrial control. Its useful range is between pH 3 and 12. It cannot be used in the presence of active oxidizing or reducing agents, and its potential depends upon a number of other factors than the pH. The electrode has been used extensively in the past but it seems to be losing favor.⁸

Electroanalysis or Metal Deposition. Under suitable conditions metal ions may be deposited quantitatively on a cathode and the amount deposited can be weighed. By a proper control of the voltage two or more metals can be separated from each other quantitatively. Much of the pioneer work in this field was done by Sand⁹ and by Edgar F. Smith.¹⁰ It is important that the deposit of metal be sufficiently firm so that there is no mechanical loss of metal during drying and weighing, and frequently precautions must be taken to avoid oxidation of the surface during drying. The time required for deposition of the metal can be shortened by employing a rotating anode or cathode and a high temperature to reduce polarization. For a fuller discussion of this subject the reader is referred to Vol. I and to the references cited above, as well as to various textbooks on quantitative analysis.

Titration End-Point Determinations. In volumetric analyses the use of indicators based on color changes has long been a common method for determining the end point in titrations. Electrochemical means are also available for determining the end point and in a number of applications have special advantages. A very important one is in the titration of colored or turbid solutions in which a color change would be masked or obliterated. There is also a closer selection of the end point on the basis of pH than with color indicators. Two general methods are available: one is a potentiometric method based on the abrupt change in the voltage of an electrode in the titration beaker when the end point is reached; the other is a conductometric method based on an abrupt change in the conductivity of the solution at the end point. The former has much wider application.

Potentiometric Titration. The solution to be titrated is used as the electrolyte in one half of the cell; the other half-cell may be any one of the various half-cells mentioned under H⁺ ion determinations.

⁸ For further information on the determination of pH the reader is referred to H. J. Creighton, Vol. I; M. Dole, *The Glass Electrode*, John Wiley & Sons, New York, 1941; W. M. Clark, *The Determination of Hydrogen Ions*, third edition, Williams and Wilkins Company, Baltimore, 1928; I. M. Kolthoff and H. A. Laitinen, *pH and Electro Titrations*, second edition, John Wiley & Sons, New York, 1941.

⁹ H. J. S. Sand, *J. Chem. Soc.*, 91, 373 (1907); 93, 1572 (1908).

¹⁰ E. F. Smith, *Electro-Analysis*, P. Blakiston's Son and Company, Philadelphia, 1912.

The calomel electrode is used very commonly for this purpose, with the connecting arm dipping into the solution in the titration vessel. The potential of the calomel half-cell remains constant; therefore, any change in the potential of the other electrode dipping into the titration vessel will appear as a change in the whole system.

The arrangement of the complete titration equipment is shown in Fig. 158.¹¹ As explained in Vol. I, the solution of acid is placed in a beaker which contains a hydrogen electrode and the side tube of a normal calomel electrode. The two electrodes are connected to

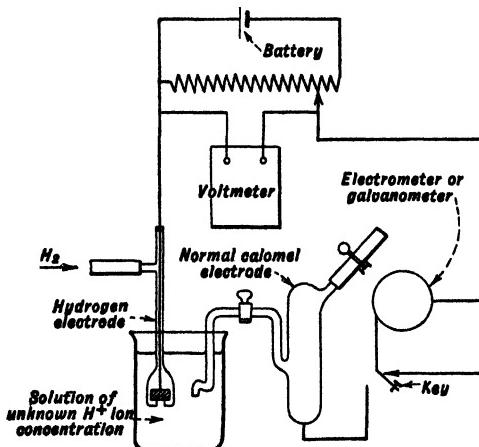


FIG. 158. Apparatus for potentiometric titration.¹¹

battery, the calomel electrode through a galvanometer or electrometer. The e.m.f. of the cell consisting of the hydrogen and calomel electrodes is balanced against a variable fraction of the e.m.f. of the battery by moving the sliding contact along the resistance, until, on depressing the contact key, the electrometer gives no deflection. The fall of potential along the wire is given on the voltmeter, and when a balance is attained this is equal to the e.m.f. of the cell. Since in a neutral solution the concentration of both the hydrogen and hydroxyl ions is 10^{-7} (see Vol. I, Chapter XVIII, the end point is reached when, at 25° C. , the e.m.f. of the above cell, and, therefore, the reading on the voltmeter, is

$$E = 0.059 \log_{10} \frac{1}{10^{-7}} + 0.282 = 0.695 \text{ volt}$$

In order to determine the amount of acid in the solution, a solution of standardized alkali is run into the beaker from a burette and the e.m.f.

¹¹ Figures 158 and 159 are based on illustrations in Vol. I.

of the cell is measured from time to time. Either the solution of the alkali is added slowly to the beaker until the voltmeter reading is 0.695 volt, or the quantity of alkali required to neutralize the acid is determined by plotting a number of voltmeter readings against the corresponding volumes of standardized alkali added to the solution of the acid, and finding from the curve the volume corresponding to 0.695 volt.

Some of the results obtained by Hildebrand¹² are illustrated by the curves in Fig. 159. It will be noticed that the curves become vertical at the neutral point, indicating an abrupt rise in the voltage.

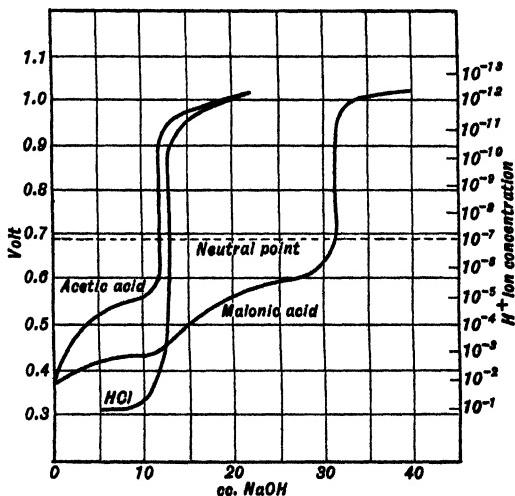


FIG. 159. Potentiometric titration curve, titrating acids with standard alkali.¹¹

If it is desired to titrate a solution to a particular H^+ ion concentration, the solution is placed in an electrode vessel with a hydrogen electrode; a second, similar vessel is prepared with a hydrogen electrode and a solution having the desired H^+ ion concentration. A table showing the composition of solutions having definite H^+ ion concentrations is given in Vol. I. The two solutions are connected with a bridge and the electrodes through a sensitive galvanometer and tapping key. The alkaline titrating solution is run into the first solution until, on depressing the key, the galvanometer gives no deflection.

In a method used by Cox,¹³ the solution to be titrated is divided into two equal portions, each placed in a suitable vessel, such as a beaker, and each supplied with a platinum electrode. The two solutions are connected by a bridge, which may be a strip of filter paper. The

¹¹ J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 847 (1913).

¹² D. C. Cox, *ibid.*, **47**, 2138 (1925).

two solutions are titrated in the ordinary way, side by side, from two burettes, but one burette is always kept 0.2 cc. ahead of the other; then, instead of measuring the potentials of the two solutions, only

their difference is noted after each addition of titrant. The difference will reach a maximum when one solution has reached the end point but the other has not.

MacInnes and Jones in a similar method use only one burette and beaker with both platinum electrodes in the same solution. One electrode is covered with a small hood so that thorough mixing is prevented after each addition of reagent, whereby one electrode is retarded.

Conductometric Titration. The end point in titrations can also be found by determining the conductivity of the solution being titrated. Conductometric methods have been studied and systematized by Kolthoff.¹⁴

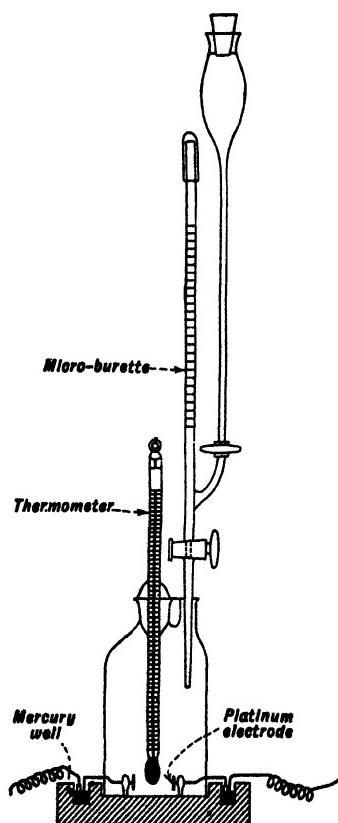
An important advantage of conductometric titrations lies in the fact that marked hydrolysis, solubility, or dissociation of the reaction product does not affect the accuracy of the method very much. Such titration methods are, therefore, used where other titration methods fail to give results. The conductometric method, however, cannot be applied as generally as the potentiometric method, because large amounts

Fig. 160. Apparatus for determining titration end points by conductance method.

of foreign electrolytes, which do not take part in the reaction, affect the accuracy greatly.

In conductometric titration the conductance is measured after addition of successive amounts of reagent from a burette. The points thus obtained are plotted to give a graph, conductance being plotted against amount of reagent added. As a rule a broken line will be obtained with a

¹⁴ I. M. Kolthoff, *The Colorimetric and Potentiometric Determination of pH*, p. 133, John Wiley & Sons, New York, 1931; *Konduktometrische Titrations*, Verlag W. Steinkopff, Dresden, 1928; *Ind. Eng. Chem., Anal. Ed.*, 2, 225 (1930).



sharp inflection at the end point. In contrast to any other titration method, measurements near the end point have no special significance.

A titration cell is shown in Fig. 160. The two platinized platinum electrodes are placed vertically in order to prevent the deposit of a precipitate in precipitation reactions. Platinum wires are sealed in the glass, one end of each welded to an electrode, the other end dipping into a mercury pocket outside the cell. A microburette is used, connected to a reservoir containing a supply of the standard solution. It is desirable to select a reagent which is at least 10 to 20 times more concentrated than the solution to be titrated. The conductivity of most salts increases about 2 to 2.5 per cent for each degree centigrade rise in temperature, so that for accurate work the titration cell should be placed in a thermostat.

For details about the measurement of electrical conductance and the significance of the cell constant the reader is referred to Vol. I.

Figure 161 shows the type of curve obtained when a strong acid is titrated with a strong base, or vice versa. This represents one of the simpler types of conductometric titrations and would be used only where a colorimetric end point would be obliterated by a colored or highly turbid solution. For conductivity curves obtained in a variety of titrations the reader is referred to the publications by Kolthoff mentioned previously.

Polarography. A method of analysis that is receiving considerable attention is known as polarographic analysis or polarography.¹⁴ A polarizing cell contains a small, easily polarizable electrode which usually consists of a slowly growing drop of mercury commonly referred to as a dropping mercury electrode, and a large non-polarizable electrode. The non-polarizable electrode may be another mercury electrode of large area or it may be a calomel electrode. The cell is connected in series with a galvanometer or millivoltmeter, a variable resistance, and a battery. The cell contains the solution to be analyzed. The applied voltage is gradually increased, and the current corresponding to each voltage is measured by means of a galvanometer or milliammeter, from which a curve or polarograph is drawn. The curve can also be produced

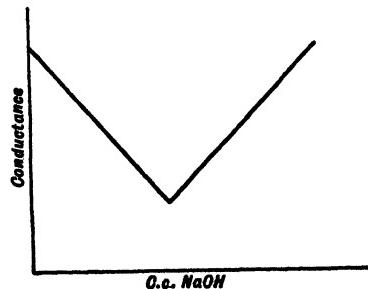


FIG. 161. Conductance titration curve when titrating a strong acid with a strong base.

¹⁴ I. M. Kolthoff and J. J. Lingane, *Polarography*, Interscience Publishers, New York, 1941; O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.*, 71, 181 (1937); O. H. Müller, *J. Chem. Education*, 18, 65, 111, 172, 227, 230 (1941).

by recording instruments which automatically plot a graph of the current against the applied voltage. A curve containing a series of steps is obtained; each step identifies a different species of cation, and the height of the step, called the wave height, is a function of the concentration of that cation. A standard solution of each ion must be electrolyzed under identical conditions for a polarograph for comparison. A limitation as well as an outstanding advantage of the system is that the method is applicable chiefly to very dilute solutions. Analysis is carried out most easily if the concentration of the solution is 10^{-4} to $10^{-3} M$.

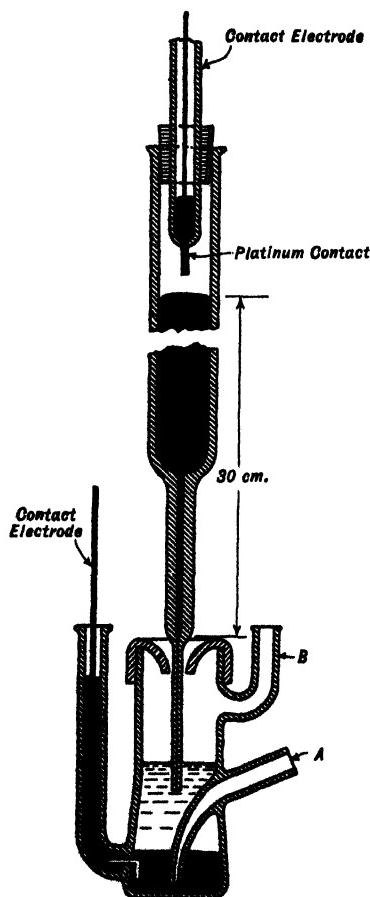


Fig. 162. A polarizing cell for polarographic analysis.¹⁷

quantities as small as a drop can be analyzed; (6) ability to analyze very dilute solutions—the method is carried out most easily if the concentration of the solution is 10^{-4} to $10^{-3} M$; (7) production of an automatic graph which provides a permanent record.

¹⁷O. H. Müller, loc. cit.

¹⁸Adapted from *The Electro-Chemograph*, Technical Publication E-94, Leeds & Northrup Company, Philadelphia, 1939.

A cross-section of a polarizing cell is shown in Fig. 162. Before analysis is started the solution is completely freed of dissolved oxygen by passing hydrogen in at the tube *A* and allowing it to bubble up through the solution. A cap on the cell protects the solution from the atmosphere while an analysis is being made, and the solution is additionally protected by passing hydrogen in at tube *B* instead of tube *A* and letting it escape through the opening in the cap.

The advantages credited to polarography are:¹⁸ (1) excellent reproducibility; (2) high sensitivity; (3) rapid operation; (4) simultaneous quantitative and qualitative analysis of several components of a solution; (5) possibility of analyzing small quantities of solution—5 to 10 cc. is sufficient, but

Conductivity Measurements. The same fundamental principles are involved in using conductivity measurements¹⁸ for analyzing solutions as in using some other physical property for the purpose, such as density, index of refraction, or optical rotation. It is necessary that the relation between conductivity and the concentration of the solution is known; it is also necessary that no other substance be present that affects the conductivity, unless this conductivity can be taken into account. The simplest application is one in which the solution contains a single ionogen whose conductivity at various concentrations is known. It is merely necessary to interpolate graphically or arithmetically in the table. If there is a maximum conductivity, two concentrations are possible for a given conductivity reading. By diluting the solution a little and recalculating the conductivity it is easy to determine on which side of the maximum the solution lies: if the dilution increases the conductivity, the concentration lies on the more-concentrated side of the maximum; if it decreases the conductivity, the concentration lies on the other side of the maximum point. If the solution has a concentration near that of maximum conductivity, the curve has a very small slope and accurate determinations cannot be made. The solution can then be diluted a known amount to bring the conductivity to a point where the curve has a greater slope and the conductivity is redetermined. The concentration of the original solution can then be calculated.

The method, in addition to being employed for determining the concentrations of solutions, has been used for calculating the impurities in sugar and in mineral waters¹⁹ and the amounts of salts in solution when the solution contains a mixture of two salts and the mixture is the arithmetical mean of the single conductivities. It has been used to analyze mixtures of potassium chloride with potassium bromide and of potassium sulphate with rubidium sulphate.

Methods of determining conductivities are described in Vol. I.

¹⁸ See F. Kohlrausch and L. Holborn, *Das Leitvermögen der Elektrolyte*, p. 131, B. G. Teubner, Leipzig, 1898; and E. A. Keeler, *Trans. Am. Electrochem. Soc.*, **38**, 113 (1920).

¹⁹ E. Reichert, *Z. anal. Chem.*, **28**, 1 (1889).

CHAPTER XV

ELECTRIC FURNACES—GENERAL

The first electric furnace of any practical importance was constructed by Siemens in 1878, and four years later he melted about 20 lb. steel and 8 lb. platinum in his furnace. This may be considered the beginning of the commercial electric furnace; since then the development has been rapid. The electric furnace, however, had its beginning at a much earlier date. Only a few months after Volta's discovery of the electric battery in 1800, Sir Humphry Davy produced an arc light between carbon points. This was the first step in the evolution of the arc furnace. Later Davy produced sodium and potassium in an apparatus that was an electric furnace on a small scale. In 1839 Robert Hare operated a small electric furnace in a vacuum under a bell-jar, using current from a battery, and produced calcium, calcium carbide, graphite, and phosphorus. However, prior to the invention of the dynamo in 1867, it was very troublesome and expensive to conduct experiments requiring any considerable amount of electrical power.

Electrical heating has certain definite applications in which it encounters no competition from combustion methods. This is especially true of processes requiring high temperatures, as the preparation of calcium carbide, silicon carbide, and graphite. For some other applications electrical heating has many advantages over combustion methods but is more expensive. In some of these processes electrical heating gives greater over-all economy, for on account of its closer heat control or greater cleanliness there is less spoilage of the product. This is true in "firing" porcelain enamel onto a metal base and in the heating of kilns for decorated china. Heat can usually be developed electrically at or near the point of use and sometimes even in the material to be heated. Smoke, fumes, dirt, ashes, and moisture are avoided. The control of the furnace can more readily be made automatic, and less attention is required to operate and maintain the equipment. Many electric furnaces can be thoroughly insulated, with a resultant reduction in heating loss. Electric heating tends to offer more comfortable, healthful, and convenient working conditions.¹

¹ For a discussion of the advantages and disadvantages of electric furnaces as compared to fuel-fired furnaces, see Trinks, *Industrial Furnaces*, John Wiley & Sons, New York, 1934, 1942.

Electric furnaces can be divided into three groups: arc furnaces, resistance furnaces, and induction furnaces.

Arc Furnaces. When there is a discharge of electricity through a gas, the current is carried by ions which consist of positively or negatively charged atoms or molecules of gas and of free electrons. The general trend of the *characteristic*, i.e., a curve showing the relation between voltage and current, is shown in Fig. 163.² The curve is not drawn to scale on account of the great range represented. The top of the brush discharge may correspond to nearly 100,000 volts, the low-tension arc to 30 volts; the current in the low-tension arc may be many thousand times as great as in the high-tension arc.

In our consideration we are particularly interested in the high-tension and low-tension arcs. The high-tension arc results from a steady increase in current from a brush discharge. At a certain point, varying with conditions, the brush discharge breaks down, sparking occurs, and the high-tension arc begins to form. It is this discharge that is most active in producing nitric oxide when burning in air; it finds technical application in fixation of atmospheric nitrogen. It will be noticed that the curve has a negative characteristic, i.e., the voltage falls as the current increases. This is because an increased current produces an increased temperature which produces a greater velocity of the current-carrying particles in the arc, and because the hot electrodes begin to emit electrons in large numbers. Therefore, if the arc is fed by a source of constant voltage and a small increase in current occurs, the arc voltage drops, and, the external voltage remaining constant, a still larger current passes. The current, therefore, tends to increase enormously, the discharge becomes unstable, sparking takes place, and the low-tension arc forms. If, on the other hand, there is a slight decrease in current, the temperature drops, the resistance rises, and since the impressed voltage is constant the current decreases indefinitely and the arc goes out. Therefore, to render the arc stable the voltage across it must be lowered simultaneously with an increase in current. This is effected by placing a resistance in series with the arc when direct current is used, an inductance when alternating current is used. An increased current then automatically increases the voltage

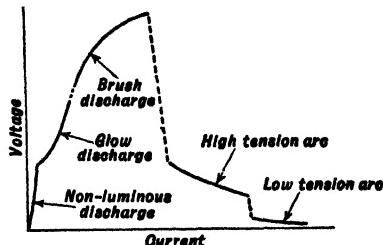


FIG. 163. Characteristics of electric discharge through air.

² G. Brion, *Z. Elektrochem.*, 14, 245 (1908).

drop across the impedance (resistance or inductance) and, therefore, increases the same across the arc.

In a high-tension arc the voltage drop is given by the equation²

$$E = a + \frac{bL}{\sqrt{I}}$$

E = voltage across the arc
 a = approx. 350
 b = 100 to 150
 L = length of arc in cm.
 I = current

The values for the constants a and b are for air at atmospheric pressure.

The temperature of the high-tension arc varies in different parts and depends upon the current and voltage relations. In the positive column it may be considered to be 2,200 to 2,500° C. (4,000 to 4,500° F.).

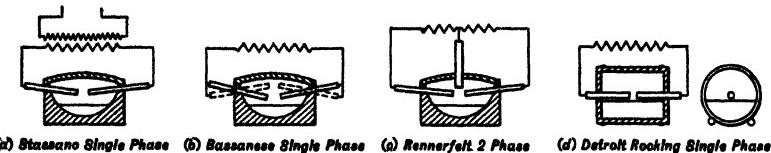


FIG. 164. Independent or indirect-arc furnaces.

The low-tension arc is used in steel and carbide furnaces. The breakdown of the high-tension to the low-tension arc is caused in part by the temperature of the electrode rising high enough to heat the charge of metals or metallic oxides to a point where they give out large quantities of electrons. Electrons are shot off from the cathode, positive ions from the anode, and their impact on the gaseous molecules increases the ionization enormously. The conductance rises rapidly, and the temperature increases very much. The temperature of the low-tension arc varies with conditions; with carbon electrodes it is about 3,500° C. (6,500° F.).

Independent or Indirect-Arc Furnaces. In the independent-arc furnaces, the electrodes are placed in the furnace above the charge. The electrodes are placed horizontally in the furnace or they dip down slightly toward the charge as in the Stassano and Bassanese single-phase steel furnaces shown in *a* and *b*, Fig. 164. In the Rennerfelt two-phase furnace, Fig. 164*c*, the arc is directed downward on the charge by a third vertical electrode.

In the independent-arc furnace the metal and slag are heated by radiation from the arc and from the hot crown above the hearth. In the region of the arc the furnace is very hot, so that near the arc the metal and slag may be overheated while near the bottom the metal will be too cold. The localized heating is very hard on the refractory

lining and the roof. With severe use a 6-ton furnace lining may last for less than 10 heats, but much longer refractory life is generally attained. A difficulty with independent arc furnaces is the liability of breakage of the horizontal electrodes. To avoid this, some users have placed the electrodes vertically through the roof.

Direct-Arc Furnaces. In direct-arc furnaces the arc is formed between the electrodes and the charge. There are two types of direct-arc furnaces, both used widely in steel making. One type, the *series arc* furnace, has a non-conducting hearth; the other has a conducting hearth. Of the latter,

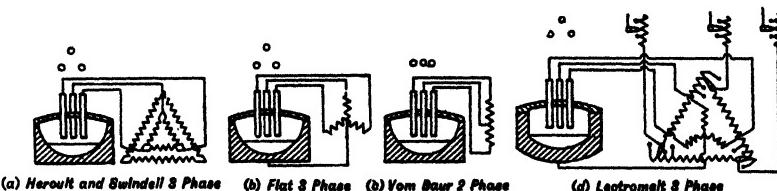


FIG. 165. Direct-series-arc furnaces.

there are two kinds. In one, a carbon block or a group of soft-steel bars or other conductor is placed in the refractory hearth to carry the current to the charge in the furnace. This is called a *hearth-electrode* furnace. In the other type the hearth may be of regular construction but become conducting when heated to a high temperature; it is called a *buried hearth-electrode* or *conducting-hearth* furnace.

Direct-series-arc furnaces are shown in Fig. 165. The Heroult furnace is a widely used type which may be considered representative. The electrodes enter the furnace through the roof, and there are as many arcs as there are electrodes, never less than two.



FIG. 166. Direct-arc, hearth-electrode furnaces.

Direct-arc, hearth-electrode furnaces are shown in Fig. 166. A conductor passes through the bottom of the hearth and makes direct contact with the charge. The Girod, Snyder, and Kaller furnaces belong to this class. A difficulty encountered in this type of furnace, when used for metallurgical purposes, is that trouble seems to develop with the bottom when the furnace is in operation, yet in a number of installations this type is giving satisfaction.

Direct-arc, conducting-hearth furnaces have proved quite practicable. The Greaves-Etchells was one of the first furnaces to apply this principle. The hearth electrode does not come through the hearth but is buried in

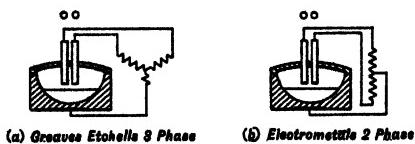


FIG. 167. Direct-arc, conducting-hearth furnaces.

it. It may consist of a heavy copper plate lying at the bottom of the hearth refractory. The Electrometals furnace also employs this type of construction. The principle of the construction is shown in Fig. 167.

Figure 168 shows diagrams of furnaces of a *mixed type* which employ more than one of the features of the above-described types.

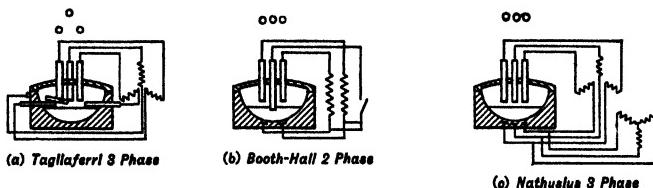


FIG. 168. Mixed types of arc furnaces.

The thermal efficiency of the direct-arc furnace is high when used for melting purposes, some furnaces averaging 75 per cent over a long period of time. Lyon⁴ and his associates give the following efficiencies of various furnaces used in the metallurgy of iron and steel:

Blast furnace	Average 60 per cent
Acid open-hearth	Average 12 per cent
Basic open-hearth	Average 10 per cent
Crucible	Average 4 per cent
Direct-arc furnace	Average 70 per cent

The main heat losses in electric-arc furnaces are those through the electrodes, the doors, and the lining. The greatest loss is through the cooling water in the roof rings and the electrode holders. Water cooling is very essential to prevent rapid destruction of electrode holders and other metal parts. The water circulating through the cooling rings and electrode holders carries away 15 to 20 per cent of the energy input to the furnace. The loss through the doors is usually less than 5 per cent. If the furnace lining is not insulated the heat lost through the furnace walls may amount to 5 or 6 per cent of the energy input. This may be much reduced by applying good insulation, but the life of the refractory lining inside is greatly shortened. It has not been definitely

⁴ D. A. Lyon, R. M. Keeney, and J. F. Cullen, "The Electric Furnace in Metallurgical Work," *Bur. Mines Bull.* 77, p. 4, 1914.

established which economy is more desirable—heat economy or economy in the refractories.

Resistance Furnaces. In resistance furnaces, heat is generated in a suitable resistance in the furnace. This may be done by means of auxiliary heating elements acting as resistors as shown in the wire-wound type of furnace, Fig. 169a. The wire is usually a nickel-chromium alloy, such as nichrome, or platinum. In some furnaces, especially larger ones, resistance grids are cast, or are Globar rods, made of silicon carbide. Carbon or graphite in granular form or in plates is also used.

Resistance furnaces may also have the resistor placed inside the charge as in silicon carbide furnaces, Fig. 169b.



FIG. 169. Resistance furnaces.

If the material to be heated is sufficiently conducting it may be used as the resistor. This is done in furnaces for producing graphite electrodes, Fig. 169c. The resistor may also be liquid as in the cell or furnace for producing aluminum and other cells using fused electrolytes.

Induction Furnaces. One type of induction furnace is essentially a step-down transformer in which the furnace charge is the short-circuited secondary coil. The furnace is subject to the same magnetic and electrical losses caused by hysteresis as a transformer. From the nature of furnace design it is impossible to bring the primary and secondary close enough together so that all the lines of magnetic flux are cut by both of them, and so these losses are greater in an induction furnace than in a transformer, which gives a lower power factor. As the power factor can be increased by using a low frequency, a frequency of 5 cycles per second is usual for this type of furnace. Figure 170a shows diagrammatically this type of furnace construction.

The low-frequency furnace was invented simultaneously by Ferranti and by Colby in 1887. The Kjellin and Röchling-Rodenhauser furnaces have attained commercial use in Europe but have not gained favor in the United States.

A difficulty encountered in this kind of furnace is that, when an alternating or direct current flows through a liquid conductor in a narrow channel, the conductor tends to contract in cross-section because of the attraction of parallel conductors carrying currents in the same direction. If there is a slight constriction in the channel and the current

is large, a depression will be formed in the metal which may be great enough to separate the metal and thus break the circuit. When this happens the metal flows together, but separates again as soon as the circuit is completed. This is known as the *pinch effect*. It precludes the use of open-channel induction furnaces for melting good conductors such as copper, brass, or aluminum, for on account of the high current in the secondary the pronounced pinch effect causes the circuit to be open such a large part of the time that the metal freezes.

This type of induction furnace is not well suited for intermittent melting service, for it is necessary to retain a circuit of molten metal from one charge to another.

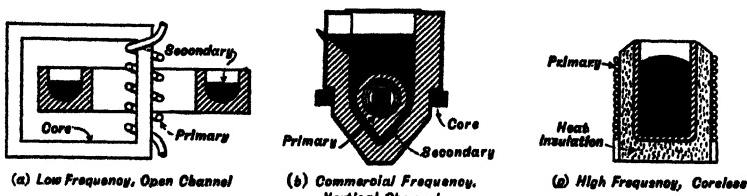


FIG. 170. Induction furnaces.

The Ajax-Wyatt low-frequency induction furnace has an enclosed vertical ring of molten metal so that the static pressure of the metal overcomes the pinch effect. This type of furnace, Fig. 170b, is widely used for brass melting.

When a liquid conductor makes a sharp bend the repulsion of the current which flows in opposite directions on the two sides of the bend causes agitation and stirring of the liquid. This is called the *corner effect*. In three-phase induction furnaces there is a rotating field which drags the molten metal after it. This is called a *motor effect*.

The use of high-frequency current with weak magnetic fields makes it possible to dispense with the iron core used in the low-frequency transformer-type furnaces, and it is unnecessary for the object to be heated to form a closed circuit in the form of a loop. This makes it possible to heat non-conducting materials in a conducting crucible. The Ajax-Northrup coreless induction furnace, Fig. 170c, is of this type. Table XXIX classifies metallurgical furnaces.

Refractories.⁴ Refractories used in the linings of electric furnaces consist of bricks and specially shaped blocks, and granular materials. Chemically they may be classed as acid, basic, or neutral materials.

⁴The following books give a fuller discussion on the subject of refractories in general: F. H. Norton, *Refractories*, McGraw-Hill Book Company, New York, 1940; A. B. Scott, *Refractory Materials: Their Manufacture and Use*, Charles Griffin and Company, London, 1924; F. T. Havard, *Refractories and Furnaces*, McGraw-Hill Book Company, New York, 1912.

TABLE XXIX

CLASSIFICATION OF ELECTRIC METALLURGICAL FURNACES

Independent arc.....	Angehrni Bassanese Booth Detroit Rennerfelt Stassano
Arc furnaces....	
Series arc.....	Arnold Booth Fiat Greene Heroult Keller Ludlum Moore Rapid Lectromelt Stobie Swindell Volta Vom Baur
Direct arc....	
Hearth electrode.....	Girod Keller Snyder
Conducting hearth...	Electrometals Greaves-Etchells
Mixed type	Booth-Hall Nathusius Tagliaferri
Induction furnaces	Ajax-Northrup Ajax-Wyatt General Electric Greene Kjellin Röchling-Rodenhauser
Resistance furnaces.....	Bailey Gin

Silica brick and firebrick (made of fireclay) are classed as acid refractories. In steel-refining furnaces silica brick are used for the upper linings and roofs in basic furnaces and for the whole linings in acid furnaces. Silica sand is used for bottom making in acid furnaces. Silica refractories are moderate in price, are very refractory, and retain

their strength quite well at high temperatures. They expand and contract considerably at medium temperatures and are thus apt to spall or to crack. The fusion point of good silica refractories is about 1,750° C. (3,182° F.).

Fireclay refractories do not find much use in furnace linings where they come in contact with very high temperatures. They find application in electric furnaces where they are protected from the high temperatures, as in the construction of silicon carbide and graphite furnaces. Fireclay is also used as a mortar for laying up other refractories and for luting openings around doors. High-grade fireclay refractories may be used at temperatures up to 1,600° C. (2,912° F.).

Magnesite and dolomite are the leading basic refractories. They are used for the linings up to the slag line in basic steel furnaces.

Magnesite refractories are considered far superior to dolomite. They are made by calcining magnesite, $MgCO_3$, to produce the oxide, MgO . Good grades of refractories are made from the crystalline variety and contain 85 per cent MgO , 6 to 8 per cent Fe_2O_3 , and under 5 per cent CaO plus Al_2O_3 . Magnesite is very refractory but it is not as strong at high temperatures or as cheap as silica. Therefore, it is not used above the slag line or in roofs. Its softening point is about 1,980° C. (3,600° F.).

Dolomite is a mixture of calcium and magnesium carbonates having, when pure, the composition $MgCO_3 \cdot CaCO_3$. It is used for repairs of basic bottoms, being added between heats.

Chrome refractories, also called chromite, contain 35 to 45 per cent Cr_2O_3 and 15 to 25 per cent FeO . It is a neutral refractory and in the form of bricks is used to separate the basic part of the lining from the acid part above it, although in some cases a chrome mortar between the two types of refractories serves the purpose quite well. The bricks are generally uniform in character but are somewhat expensive.

Silicon carbide, SiC , and fused alumina, Al_2O_3 , are also classed as neutral refractories. They are characterized by their exceptional refractory properties and mechanical strength at high temperatures, and have sometimes been classed as "super refractories." These materials are themselves products of electric furnaces, and their preparation is discussed later, beginning on pages 443 and 449, respectively. Mullite, $2Al_2O_3 \cdot 3SiO_2$, sometimes called sillimanite, has also found successful application as a neutral refractory in electric furnaces, and is likewise an electric-furnace product.

Electric-furnace refractories should have a high softening point, for use in arc steel furnaces preferably above 1,700° C. (3,092° F.). They should have high mechanical strength at high temperatures; and where they come in contact with slag they should have what is generally

called a high density, though what is really meant is a low porosity. If the slag can enter the porous structure of a refractory brick, the brick is likely to disintegrate rapidly. The coefficient of expansion should be low in such furnaces as arc furnaces, where the opening of a charging door allows a large in-rush of cold air into the furnace. In arc furnaces a low coefficient of expansion is also desirable, for the temperature rise when a cold furnace is started may be as much as 500° C. (932° F.) an hour. If the coefficient of expansion of the refractory is not low, cracking and spalling will result. The refractory should have high resistance to corrosion and to abrasion. From the point of view of conserving heat energy, the refractory should possess low heat conductivity, but this may cause overheating of the refractory, which will shorten its life. Therefore, in some furnaces even insulating materials are used to help retain the heat, whereas in others the refractory lining has been made thin purposely to aid in conducting away the heat. A low electrical resistance is desirable in the upper lining to avoid current losses through it if electrical contact is made with it.

Electrodes. It has been aptly remarked that the development of the carbon electrode is so inseparably linked with the advancement of the electric furnace that it cannot be said that one led while the other followed. The raw materials for electric-furnace electrodes are essentially anthracite coal and petroleum coke, with some tar and hard and soft pitch as binding materials.

The anthracite coal is carefully selected and washed and then crushed. It is calcined in special retorts or calcining furnaces; for producing highest-grade materials electric calcination furnaces are used. The calcination drives off all the volatile gases and oils, and reduces the electrical resistance of the material.

Petroleum coke is also crushed and calcined, but the calcination is not carried to as high a temperature as with the coal. After cooling, both materials are further crushed and then weighed into mixers with the correct proportion of bonding material.

For the smaller sizes of electrodes and the long lengths of the larger sizes the hot mix is placed in a press and then extruded through dies. Large-size electrodes are also molded or tamped. The mix is shoveled into steam-jacketed steel molds and packed down with an automatic ram. When the mold is filled, it is put under high pressure to compress the material to its maximum density.

After being formed, the "green" electrodes are baked at a temperature of about 1,000° C. (1,832° F.) to drive off all the volatile from the bonding material. As the electrodes soften while baking they are supported by packing in fine coke or sand. When the baking is completed,

the electrodes are allowed to cool very slowly to prevent unequal cooling strains. The baking and cooling combined require several weeks.

As the electrodes become shorter in service by the burning off of the hot ends, new sections are attached to the old by means of threaded dowels or connecting pins. Each electrode has a female thread on each end; a threaded connecting pin fits into this thread as shown in Fig. 171a and b. In order to reduce the electrical resistance of the joint, a joint compound is used for carbon but not for graphite electrodes. This consists of finely divided carbon or graphite made into a paste with water, with or without other additions.

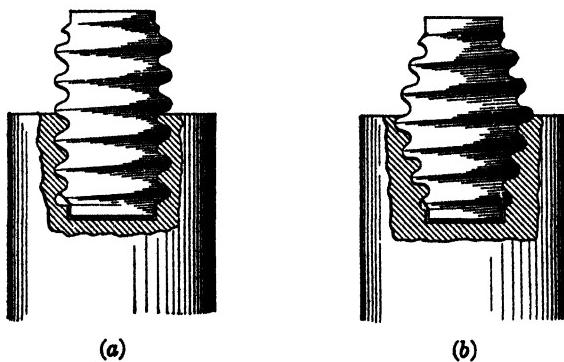


FIG. 171. Dowel pins for connecting electrodes.

In a number of furnaces graphite electrodes are used. They are formed by heating the baked carbon electrodes to a temperature of $2,200^{\circ}$ C. ($3,992^{\circ}$ F.) or higher in an electric resistance furnace. This graphitization is discussed more fully as an electric-furnace process, beginning on page 452.

The relative advantages and disadvantages of graphite over amorphous carbon electrodes in arc furnaces have been summarized by Sisco.⁶ In favor of the graphite electrodes is the fact that, their conductance being four times that of amorphous carbon, the electrodes need be only half the diameter. The smaller electrodes permit a stronger roof construction, do not require as heavy a control mechanism, have but half the transportation cost, and are removed more easily if they break and fall into the bath. Graphite electrodes have no resistance losses at the joints and require no electrode joint compound. Owing to their greater resistance to oxidation, the consumption is less than half that of amorphous carbon electrodes.

⁶ W. T. Sisco, *The Manufacture of Electric Steel*, p. 65, McGraw-Hill Book Company, New York, 1924.

Among the disadvantages of graphite electrodes compared to amorphous carbon electrodes is that they are more expensive per pound of electrode (but not necessarily per ton of steel), so that, if breakage occurs in transportation or handling, the loss is greater. Also, since they are more fragile, they break more easily. They have a higher heat conductivity, so that they cause greater heat loss than amorphous carbon electrodes.

There is a gradual tendency toward the use of graphite electrodes in steel furnaces. They are smaller and can be placed near the center,

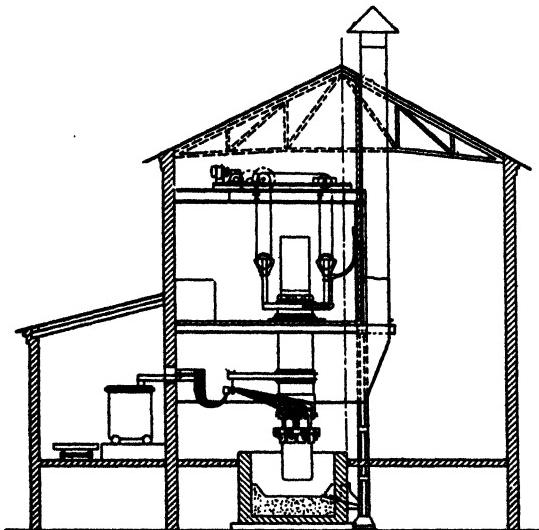


Fig. 172. Soderberg continuous self-baking electrode.

and bore only one hole through the charge when melting cold scrap. Graphite electrodes are used exclusively for furnaces of 15-ton capacity and above. Carbon is seldom used for electrodes above 17 in. in diameter, but on account of its superior mechanical strength it is used for electrodes under 8 in. in diameter.

The Soderberg continuous electrode has found favor in a number of furnace installations. An electrode shell is made of a sheet-iron casing of small gage, having ribs extending radially to the center. An electrode mixture of about the same composition as used for ordinary carbon electrodes is tamped into the metal shell. As the electrode is slowly fed downward into the furnace the green mixture becomes baked, so that the part of the electrode below the holder is a solid carbon electrode encased in a steel jacket. When new electrode material is needed, a new section of steel casing is welded to the top of the old

and filled with the mixture. The top of the old electrode is still soft so that the two parts mix and become one solid unit during the subsequent baking. The steel casing is fed into the furnace as part of the electrode.

The continuous self-baking electrode is economical, has less heat loss and oxidation and better conductivity than the conventional type, and is free from electrode breakage. It has found its greatest application in the non-tilting ferroalloy furnaces, but has also been applied successfully to tilting steel furnaces. Figure 172 shows the method of applying the electrode.

Voltage. The voltage required for an electric furnace depends upon the type of furnace, its design, the nature of the charge, and the capacity of the furnace. For example, a 3-ton steel-melting furnace of the direct-arc type, 2,000 kv-a. capacity, producing basic ordinary carbon steels, operates with the electrodes practically touching the slag and will therefore require a relatively low voltage, namely 90 to 95 volts for load and 95 volts no-load. In producing stainless steel in the same furnace, it is necessary to keep the electrodes higher above the melt to avoid the possibility of introducing carbon into the charge. The load voltage will be 105 to 115 volts; the no-load voltage, 115 volts. In basic melting, the slag on the steel is thicker and more viscous and has a higher resistance. The furnace will then require 125 to 130 volts for operation with a no-load voltage of 130 volts.

For larger furnaces the arc lengths remain about the same as in the smaller ones and the slag conditions are similar. However, a greater energy input is necessary, which requires a higher no-load voltage. For a 25-ton furnace producing basic carbon steel this is about 110 volts, for stainless steel 130 volts, and although such large furnaces are rarely used for basic operation, the corresponding voltage would be 150 to 160 volts.

CHAPTER XVI

ELECTRIC FURNACES IN THE METALLURGICAL INDUSTRIES

The chief application of electric furnaces in metallurgy is in steel refining, or, as it is frequently called, the production of "electric" steel, which includes the manufacture of a variety of alloy steels as well as ordinary carbon steels of high purity. The desire to produce a product to compete with "crucible" steel stimulated development of electric steel furnaces, and the venture has proved so successful that electric steel now is employed for many purposes for which crucible steel was formerly used.

But before the manufacture of electric steel, the electric-arc furnace had proved its worth in the manufacture of ferroalloys, such as ferrosilicon and ferrotungsten, utilized in the manufacture of alloy steels. The high temperature necessary for the production of these alloys gives electric melting special advantages, and today the electric furnace has the field of the manufacture of ferroalloys practically to itself. However, electric furnaces are or have been used successfully in a number of other metallurgical applications, such as the reduction of iron ore, the manufacture of gray cast iron and of "synthetic" pig iron, and in brass melting. Some of these processes are discussed in the following pages.

THE REDUCTION OF ORE

The reduction of iron ore in electric furnaces has proved successful where electrical energy is cheap; where fuel, particularly metallurgical coke, is expensive; where good iron ore is plentiful; and where iron would have to be transported great distances to supply the local demand. Electrical energy must substitute two-thirds of the coke of the blast furnace, which makes the process too costly for general adoption. Electrothermic iron-ore smelting is practiced in Sweden, Norway, Italy, and Japan.

In America electric reduction furnaces are being used mainly for reduction of non-ferrous ores.

The Stassano Reducing Furnace. Major Stassano, an Italian army officer, was the first person to reduce iron ore in an electric furnace on a commercial scale. His preliminary work was carried out in Rome in 1898 in a 150-hp. furnace shown in section in Fig. 173. It resembled an

ordinary blast furnace. A difficulty encountered in an electric ore-reducing furnace is that no reducing gases are obtained from the combustion of carbon as in the blast furnace. In the Stassano furnace the reducing action was obtained by grinding the iron ore and carbon finely, mixing them, and forming briquettes with pitch as a binder.

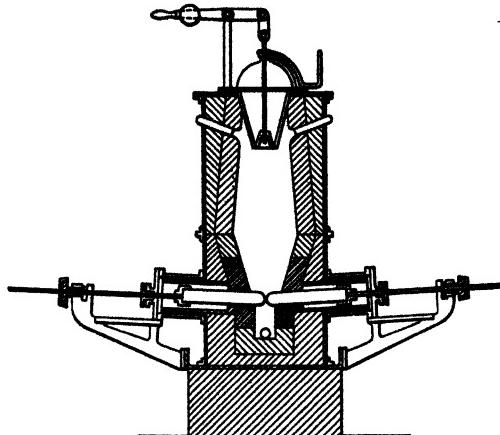


FIG. 173. Sectional elevation of early Stassano furnace for iron ore reduction.

The Electrometals Furnace.¹ More information is available on the Electrometals furnace² than on other types that have been used for the electrothermal reduction of iron ore. The furnace used at Domnarfvet, Sweden, is shown in section in Fig. 174.³ This type of furnace is built in capacities of 10,000 to 20,000 tons per year, which is about one-tenth the capacities of modern coke blast furnaces. There are 4 to 8 graphite electrodes per furnace; they are 24 to $27\frac{1}{2}$ in. in diameter. The electrode consumption is approximately $17\frac{1}{2}$ lb. per ton of iron produced.

The crucible does not support the shaft but the shaft rests on six columns, only one of which is shown in the illustration.

The furnace is operated on 24-cycle, three-phase alternating current, 20 to 80 volts. The carbon used for reduction may be either charcoal or coke; charcoal has a higher resistance than coke, which lowers the power consumption per ton of product and increases the output. The amount of charcoal consumed is a little above 800 lb. per ton of pig iron

¹Also called the Gronwall and Domnarfvet furnace.

²J. Bibby, *Engineering*, 107, 649 (1919); G. Stig, *Chem. & Met. Eng.*, 28, 29 (1920); J. Hertenius, *ibid.*, 24, 108 (1921); and G. deGeer, *ibid.*, 24, 429 (1921).

³Reproduced with permission from W. Rodenhauser, J. Schoenawa, and C. H. West Baur, *Electric Furnaces in the Iron and Steel Industry*, John Wiley & Sons, New York, 1920.

produced, which is about one-third the amount of fuel used in ordinary blast-furnace smelting.

The fuel mixed with ore serves as a conducting medium for the current. There is some arcing at the electrode ends, but the main heat is produced by resistance heating. At the high temperature the carbon reduces

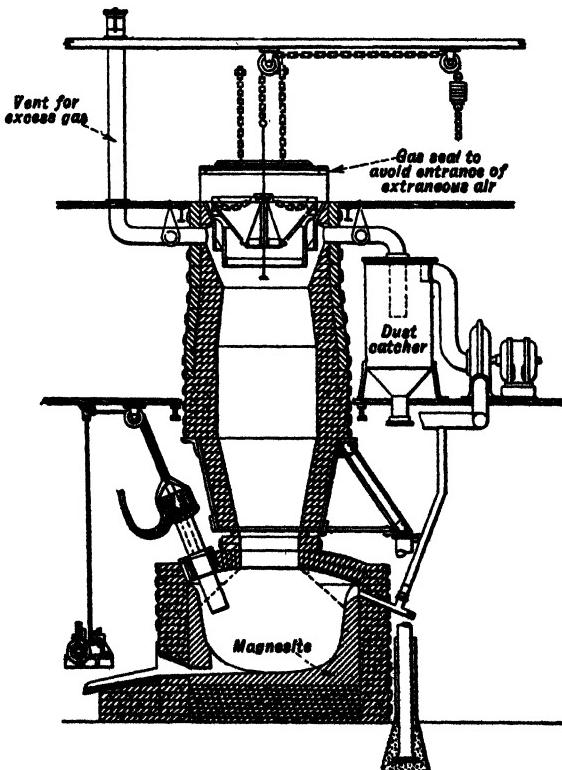


FIG. 174. Sectional elevation of shaft furnace for iron-ore reduction, at Domnarfvet, Sweden.¹

the ore with the formation of carbon monoxide and carbon dioxide. The hot gases pass through the charge in the furnace shaft, thus preheating the charge and reducing a portion of the ore. Part of the gases are cleaned and returned to the crucible where they are blown under the roof as shown. This is necessary to increase the life of the refractory lining; by cooling the roof of the crucible in this manner it will last a year with but slight repair.

It is very important to adjust quite closely the amount of reducing carbon used to the amount of oxygen in the ore. Any carbon in excess of the theoretical amount causes "hot runs." This is indicated by an

increase in the temperature of the hearth, a decreased rate of melting, and an increased ratio of carbon dioxide to carbon monoxide in the gases. As a consequence the melting zone travels upward into the shaft of the furnace, the hearth becomes too cold, and reduction ceases.

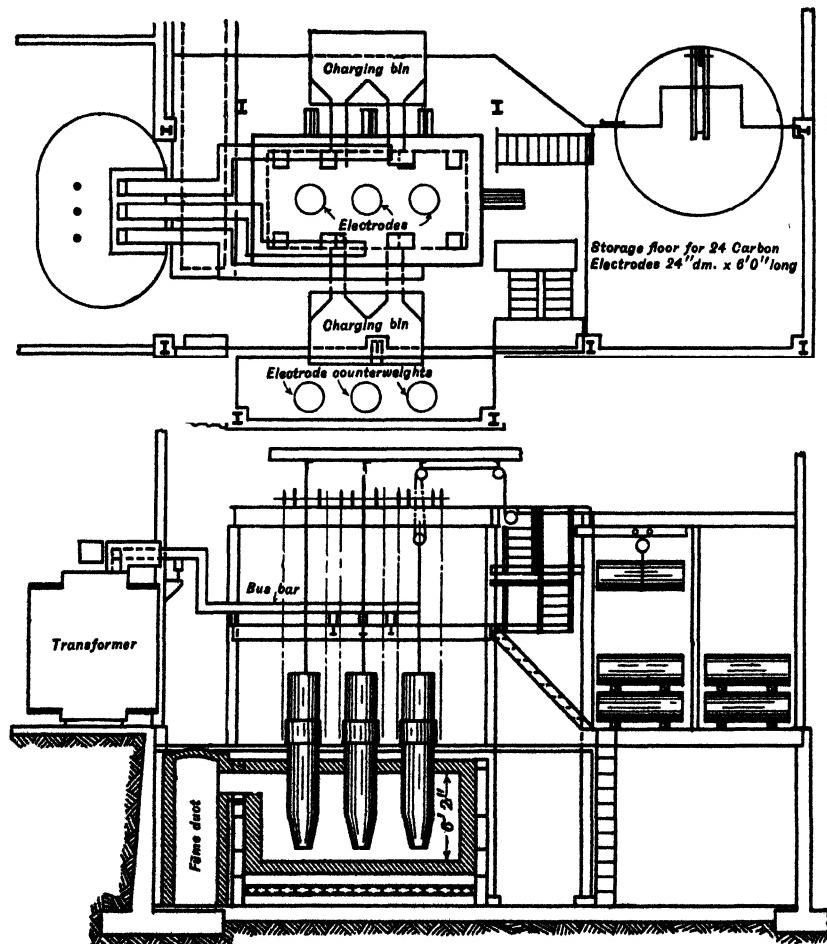


Fig. 175. Electric ore reduction furnace.

If too little carbon is used for reduction, the carbon monoxide content of the gases increases, the rate of reduction is increased, but there is insufficient heat to keep the iron molten.

The sulphur in the iron can be kept under 0.02 per cent. The power consumption is 1,750 kw-hr. per long ton of iron produced.

Non-Ferrous Reduction Furnaces. A furnace used in the United States for the reduction of non-ferrous ores is shown in Fig. 175. Like

most reduction furnaces it is patterned after the Spigerwerk furnaces in Oslo, Norway. It is essentially an oblong furnace with an arched roof, three electrodes in line entering through the roof. The charge is introduced through the roof along the side walls, and the furnace operates with the electrodes deeply submerged in the charge. Separate tappings are made of the matte and the slag. Electric reverberatory furnaces have been in operation without refractory repair in seven years. Norway and Sweden are especially advanced in the electric-furnace reduction of ores.

ELECTRIC STEEL MAKING

The superiority of the electric furnace in steel manufacture lies in the fact that a much purer steel can be produced with its aid than without it. It is true that the crucible process has long produced a steel of excellent quality, but its operation is costly and the steel is made in small batches so that large ingots must be formed by pouring several crucibles into one mold with resultant non-uniformity. In the production of electric steel, the electric furnace does not replace the Bessemer converter or the open-hearth furnace, but supplements them.

The electric furnace is used chiefly in two different ways in steel production. In the hot-metal process it receives moderately pure liquid steel from the open-hearth furnace for superrefining. In the cold-scrap process scrap steel is melted and refined in the electric furnace. Electric furnaces may be used to produce steel ingots for rolling mills, and also for making steel castings, the latter generally being referred to as steel foundry work. In 1940, of the total of more than 525 electric steel furnaces in the United States, 320 were installed in steel foundries.

In 1941 there was produced in the United States approximately 2,870,000 tons of electric steel, which was 3.46 per cent of the total steel production. In the production of alloy steel, electric furnaces accounted for 35 per cent of the total. The percentage distribution of steel production was as follows:

	PER CENT
Open-hearth	89.8
Bessemer	6.7
Electric	3.5
Other steels	Less than 0.01

Hot-Metal Process. In the refining of liquid steel, the process is carried as far as possible in the open-hearth furnace; liquid steel is then poured into the electric furnace where the sulphur is reduced to a harmless point and slag inclusions and gases are eliminated. The sulphur content of the steel when it reaches the electric furnace should be under

0.08 per cent, or its reduction in the electric furnace will be expensive and wasteful of time. The phosphorus should likewise be low, for, although it can be eliminated in the basic electric furnace, the process is costly. Phosphorus should first be eliminated in the basic open-hearth furnace. In one variation of the "Triplex" process the liquid metal goes from the Bessemer converter to the open-hearth furnace and thence to the electric furnace for final refining.

The liquid from the open-hearth furnace is poured into the electric furnace, special care being taken that no open-hearth slag is transferred. Lime is a necessary addition for slag making in the electric furnace; it is mixed with about 20 per cent of its weight of fluorspar, CaF_2 , and about an equal amount of sand, to make the slag fluid. The amount of slag added is 2 per cent or less of the weight of the bath. If it is desired to increase the carbon content of the steel, anthracite coal is added to the charge.

The open-hearth steel usually chills over the top after it is charged into the electric furnace; therefore, the furnace is first set for high temperature, and all the charge becomes molten again in a period of one-half to one hour. When the metal and slag are melted, a sample is taken for analysis. In order that the steel may be properly deoxidized, coke dust is added. Calcium carbide is formed in the furnace by the action of lime and carbon at the high temperature of the electric arc:



The carbide slag degasifies the steel and removes sulphur. Coke and lime may have to be added at intervals, and if the bath is large, it may have to be stirred. It is desirable that the furnace doors be kept closed and luted with clay to aid in maintaining the temperature.

After the steel is deoxidized the various ferroalloys may be added, such as ferrochrome, ferromanganese, ferrosilicon, and ferrovanadium, but nickel, if required, can be added as soon as the bath is melted. The bath is kept liquid and as quiet as possible, and lies dead for the last 45 minutes in order to permit slag inclusions to separate.

The heat is tapped at a temperature of 200 to 250° C. (392 to 482° F.) above its melting point, but is allowed to drop about 100° C. in the ladle. The steel must be tapped from underneath the slag.

The total time of a heat from charging the liquid metal to tapping is about 4 to 5 hr.; the power consumed is 100 to 200 kw-hr. per ton of steel produced.

The practice of charging electric furnaces with liquid steel for refining appears to be losing favor. This is largely due to the difficulty encountered in having the liquid steel ready when the electric furnace needs to

be recharged and partly to a feeling in the trade that remelted steel results in a better product. Practically all steel-refining furnaces are charged with cold steel.

Cold Scrap Process. The electric furnace finds considerable application for melting and refining scrap steel.

If the scrap contains less than 0.08 per cent phosphorus and 0.02 per cent sulphur, a very high-grade steel can be produced. This is because the stock is melted under reducing, instead of oxidizing, conditions. If a less pure stock is used a period of oxidation is necessary prior to the deoxidation, desulphurization, and degasification; the oxidation period leaves the metal with impurities which are never completely removed.

In the melting of relatively pure scrap, lime is charged upon the magnesite hearth to protect it. The scrap is then charged, and the current is turned on; it may be necessary to regulate and feed the electrodes manually, for the scrap melts away from the arc, causing difficulty in regulating the arc and maintaining a regular power input. Quite commonly relatively high voltage is used during melting, with low voltage during the refining. Coke is added to keep the slag in a deoxidized condition. Sand or fluorspar is added to the lime to liquefy the slag. This process of melting and refining is used commonly for tool steels and magnet steel containing chromium, tungsten, vanadium, and other alloying metals, and it is very important not to oxidize any of these costly materials.

The time of melting and refining pure stock is usually under 6 hr. With the exercise of care the power consumption can be kept under 800 kw-hr. per ton of steel produced.

If the scrap contains more than 0.02 per cent sulphur and 0.08 per cent phosphorus, it must be subjected to an oxidizing period. Although the melting of impure scrap does not produce as high-grade steel as the melting of pure scrap, the process has the advantage that the scrap is cheaper.

Limestone is placed on the hearth, and the charge mixed with iron ore is added. The limestone and iron ore form the "black slag," which is oxidizing. Silica and calcium fluoride may also be added to make the slag more fluid. The power is turned on, and manual regulation of the electrodes may be desirable for a time. The iron oxide removes carbon as carbon monoxide; the phosphorus is oxidized to the pentoxide and dissolves in the slag. Sulphur is present as the sulphides MnS and FeS, both of which are soluble in the slag and in the metal bath, but the relative amount in the slag increases with temperature and the basicity of the slag. In order to remove the sulphur completely it must be converted to a sulphide that is soluble in the slag only. Calcium sulphide,

CaS , fulfills this requirement but it will not form when the slag is rich in iron oxide, for iron sulphide, FeS , will form instead. Therefore, to remove sulphur the black slag containing phosphorus is removed, and a reducing slag is melted in its place. The furnace is tilted slightly, and the black slag is poured off with the aid of rabbling. If the slag is too fluid to follow the rabble it is thickened with lime. It is important that the black slag be completely removed or phosphorus will go back into the iron when the reducing slag is added.

A reducing slag, called "white slag," is then added. It consists of lime thinned with fluorspar, CaF_2 , or sand, or both, with the addition of a reducing agent which may be carbon (coke) or calcium carbide. The sulphur is removed as calcium sulphide and may be reduced to 0.001 per cent. The reducing slag also is used to remove oxygen from the steel. This action is called "degasification." The reducing slag does not effect complete degasification, and usually some ferrosilicon or ferromanganese is added to the melt. If still more complete degasification is desired a small amount of aluminum is placed in the ladle into which the steel is poured from the furnace.

Before the metal is poured the power is shut off for some 10 to 15 minutes before tapping, while the metal lies quietly in the furnace. During this "killing" period the temperature drops from about $1,700^\circ \text{C}$. ($3,092^\circ \text{F}$.) to about $1,600^\circ \text{C}$. ($2,912^\circ \text{F}$.), and, as a final cleansing, non-metallic inclusions rise through the metal to the slag.⁴

A variety of electric furnaces are used in the production of electric steel. In 1941 there were in active establishments in the United States 207 electric steel furnaces having a combined annual output of 2,870,000 net tons.

Some of the leading furnaces used in ferrous metallurgy other than ore reduction are discussed in the following pages.

FURNACES FOR STEEL MAKING

Independent-Arc Furnaces

Independent-arc furnaces have not found extensive application in the United States, but they are used in Europe. As previously mentioned,

⁴ For a more complete discussion of the chemistry of the slagging processes, and variations in the methods of operation, the reader is referred to works on metallurgy, such as H. M. Boylston, *An Introduction to the Metallurgy of Iron and Steel*, John Wiley & Sons, New York, 1926; F. T. Sisco, *The Manufacture of Electric Steel*, McGraw-Hill Book Company, New York, 1924; B. Stoughton, *The Metallurgy of Iron and Steel*, McGraw-Hill Book Company, New York, 1934.

there is local overheating of the slag and metal under the arc, while at the bottom of the charge the metal may be solid. The horizontal electrodes break easily. The furnaces have the advantage that the arc burns whether the furnace is charged or not, so that the hearth may be sintered by electric heat and kept hot for any length of time. However, the Detroit independent-arc furnace, page 423, originally designed for non-ferrous melting, is finding considerable application in ferrous metallurgy.⁵

Stassano Furnace. The Stassano is the oldest of this type of furnace in use.⁶ The electrodes are usually three, of small cross-section, and symmetrically arranged around the furnace of circular horizontal section. Three-phase alternating current is used, the transformer connection being delta. Each electrode is fastened to a metal rod which works through a cylinder and is hand-regulated by a special hydraulic arrangement; no part of the electrode is exposed to the air. The gas outlet in the roof is water-sealed so that the atmosphere in the furnace is strongly reducing. Therefore, the electrode consumption is small, and high current densities of 130 to 194 amp. per sq. in. (20 to 30 amp. per sq. cm.) can be used. The melting chamber is lined with dolomite, the domed roof with magnesite bricks. The furnace rotates slowly about an axis inclined 7° from the vertical as shown in Fig. 176. The furnace operates very smoothly. A 200-kw. furnace takes about 1,100 amp. at 110 volts.

Bassanese Furnace. The Bassanese, developed in Italy, is a modification of the Stassano furnace. The electrodes may be inclined at various angles, so that the arc may be made free burning or may be projected directly on the metal. The voltage required is higher than for the Stassano.

⁵ For a more complete discussion of electric steel making, the reader is referred to W. Rodenhauser, J. Schoenawa, and C. H. Vom Baur, *Electric Furnaces in the Iron and Steel Industry*, John Wiley & Sons, New York, 1920; and F. T. Sisco, *The Manufacture of Electric Steel*, McGraw-Hill Book Company, New York, 1924.

⁶ E. Stassano, *Electrochem. Met. Ind.*, 6, 315 (1908); *Trans. Am. Electrochem. Soc.*, 15, 63 (1909).⁷

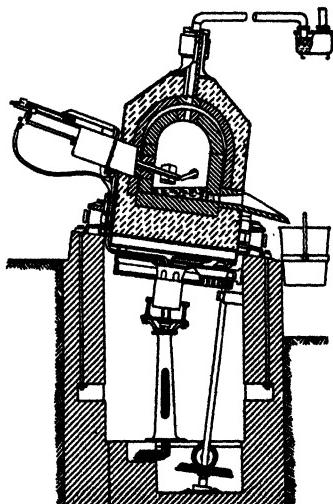


FIG. 176. Elevation of a 1-ton Stassano independent-arc furnace for steel making.

Angelini Furnace. This furnace is another modification of the Stassano. The electrodes may be so adjusted that arcs may be formed above the metal surface or between each electrode and the metal. A higher-voltage single-phase current can, therefore, be used than in other designs.

Rennerfelt Furnace. The Rennerfelt was developed in Sweden, and its use in Europe has become quite widespread; ⁷ it was introduced into America during the first World War. It differs from the Stassano furnace in that it uses two-phase current obtained from a three-phase high-tension supply by Scott connections; a third electrode introduced vertically through the roof takes the return current from both phases to the transformer. The effect of this particular arrangement is to cause the arcs to be deflected downwards magnetically toward the bath. The furnace shell is cylindrical, lined with firebrick and then usually with dolomite; the crown is lined with silica brick. The graphite electrodes are up to 6 in. in diameter, and pass through copper or bronze water-cooled cylinders at the points of introduction in the furnace. The vertical electrode can be lowered and the side electrodes tilted in a vertical plane so that the arc can follow the charge as it melts and sinks in the furnace. Large furnaces, above 6-ton capacity, are oval in shape and have two sets of electrodes of three each. Ratings are 400 kw. per ton or under. A 3-ton furnace will take 3,000 to 5,000 amp. per side electrode at 100 to 110 volts. The current density per side electrode is 150 to 250 amp. per sq. cm. (24 to 40 amp. per sq. dm.). The vertical electrode carries about 40 per cent greater current than the side electrodes and is made correspondingly larger.

Direct-Series-Arc Furnaces

Heroult Furnace. The Heroult furnace is one of the most popular and well-known electric steel-making furnaces. It was invented in 1900 by Paul Heroult. In his earlier attempts Heroult used a bottom electrode (hearth-electrode), but it was not successful and he turned to the present design. It was the first successful attempt at melting and refining steel by direct arc in a furnace with a non-conducting hearth.

Heroult furnaces are built in sizes from $\frac{1}{2}$ - to 100-ton capacities. The larger sizes are oval in horizontal section, with six electrodes; other sizes are round in section and have three electrodes. Furnaces of 50-ton capacity and larger are mainly used for refining molten metal.

⁷C. H. Von Baur, *Trans. Am. Electrochem. Soc.*, 22, 497 (1916); 21, 87 (1917); E. A. DeFries and J. Hertenius, *Iron Age*, 103, 190 (1919).

Half-ton furnaces tilt on trunnions; the larger sizes tilt on rockers as shown in a typical cross-section view, Fig. 177. Rocker tilting has the

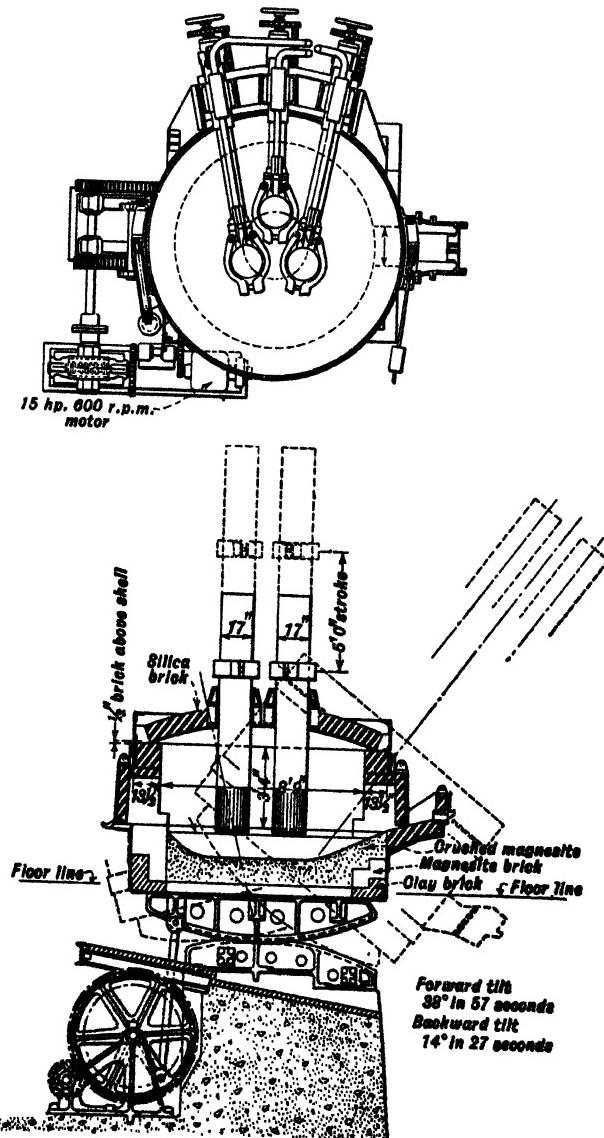


FIG. 177. Section and plan of a 7-ton Heroult furnace.

advantage that the center of gravity of the unit travels in a horizontal line when the furnace is tilting, and can be made for either front or side tilt.

The following information is supplied through the courtesy of the American Bridge Company:

Basic steel heats can be made in from 2 to 4 hours, depending on the refining period and the grade of steel desired. Acid steel heats can be made in from $1\frac{1}{2}$ to $2\frac{1}{2}$ hours. This applies to all Heroult furnaces; for charging the furnace cold scrap must be used. These furnaces cannot be charged with ore and it is inadvisable to charge with pig iron on account of the excessive cost of breaking down pig iron by electric current.

A supply of water, about 30 lb. pressure, must be available for the transformer electrode holders and roof collars. About 35 gallons per minute is required. Graphit electrodes are those most commonly used; carbon electrodes are also used.

The furnace linings for basic operation are of magnesite brick up to the slag line; silica brick on the sides above the bath and silica in the roof. For acid operation silica brick is used throughout.

The furnace consists of the following items:

The shell with structural and cast parts attached, two top rings, doors and door lifting devices, electrode holders (without electrodes), roof coolers, tilting mechanism, winches for lowering and raising electrodes, gear guards, apron under furnace for protecting the tilting mechanism and lifting plug for handling electrodes.

The electrical equipment includes a transformer, usually water cooled, connected delta on secondary and arranged for delta or Y connection on the primary giving a secondary voltage ranging from 290 to 90 volts, depending upon the transformer capacity and whether basic or acid operation is indicated. On lower capacities reactors are utilized and the switching is accomplished by motor-operated tap changers to give a choice of four or more at the will of the operator.

Standard arc regulators are used together with a switchboard for controlling electrically operated circuit breakers and tap change mechanism, three ammeters, voltmeter, voltmeter switch, polyphase meter, wattmeter and watt-hour meter, necessary relays and ground detector lamp and in some cases drawing wattmeters are standard equipment.

The electrode motors must be d.c. operated on account of dynamic braking and are usually fed from shop 230 volt d.c. supply. Alternating or direct current motors can be used for tilting.

The electrical equipment is based on any primary voltage from 2,000 to 22,000, 3-phase, 25, 50 or 60 cycle current. We do not recommend the installation of an electric furnace where current on the incoming line is less than 2,000 volts, as small voltages common for shop usage mean prohibitive electrical equipment.

The transformer should be placed in a well-ventilated room or vault, and separated from the furnace room by a wall, and it should be placed as close to the furnace as the maintenance of satisfactory operating conditions will permit. To accomplish this and to make the bus connections as short as possible, the transformer may be either mounted on a pedestal or the vault may be made in two stories. The oil switch and instrument transformers should also be placed in the transformer vault.

In selecting a location for the panels local conditions are again to be considered, the main points to be borne in mind being that the panels should be placed at a point near the furnace so that the operator can obtain a clear view of the position of all the electrodes and electrode arms; that they may be protected from water, oil and dirt, so far as possible; that they must not be subjected to vibration; and that they must not be placed in close proximity to flexible cables or leads carrying heavy

currents, as the indications of the instruments would be affected by the fields induced by these currents. In most cases, setting the panels in the front wall of the transformer vault has proved very satisfactory, but in cases where dirt and dust are serious factors it is sometimes desirable to put the regulator panel in the transformer vault and the metering equipment and control in the furnace room.

Operation: In order to illustrate the working of the furnace and the electrical operation, the melting of a heat will be outlined. For charging the furnace the electrodes are raised to their highest position by throwing over the operating switch to hand operation and using hand lever for the upward motion. After the furnace is charged the taps are set on some intermediate voltage and the main oil switch is closed. The transformers and the electrodes are now alive, the voltmeter shows the voltage and the three lamps connected between the bath (ground) and the electrodes are dimly lit. The electrodes are lowered by the hand lever until one of them touches the scrap. This is noticed on the board in that the corresponding lamp becomes dark and the other lamps become much brighter. The two electrodes which are still above the scrap are further lowered until an arc is established and current starts to flow. The lamps will vary in intensity as the arc is struck. The switch under the hand lever is now thrown over to automatic control and the electrode motors are controlled by the contact-making ammeters, which aim to maintain a constant current in the electrodes, corresponding to the setting of the power-regulating dials. Soon the meters become steady and the power is raised to the maximum by switching to a high voltage tap. The melting of the scrap now proceeds rapidly, at first chiefly under the electrodes where the arcs are buried in the scrap. During this stage, the tips of the electrodes are near the bottom of the furnace. After a while, a bath of molten metal is formed, and the electrodes raise slowly, keeping just above the level of the bath, until finally the whole heat is melted. Intermediate voltage is used for breaking up the second slag, the low voltage for refining. The power is then regulated to suit the metallurgical requirements until the heat is finished, when the electrodes are slightly raised, the oil switch thrown out and the furnace tilted to tap the heat.

Heroult furnaces are used for refining liquid steel and steel scrap and for making ferroalloys and cast and malleable iron. In basic operation the power consumption in a 15-ton furnace is 500 kw-hr. per ton of charge; in acid operation it is less than 500 kw-hr. per ton of charge, cold scrap being used in both instances. Graphite electrode consumption is 9 to 12 lb. per ton of charge. Figure 178 shows an installation of a 100-ton furnace for steel melting.

A Heroult furnace with a tilting top is shown in Fig. 179. The crown and electrodes tilt out of the way to permit rapid charging from a drop-bottom bucket carried by a crane.

Moore Rapid Lectromelt Furnace. This furnace is another widely used electric furnace. It has found extended application in steel and iron foundries and in rolling-mill plants. It was developed to the point of commercial practicability in 1916. Its advance has been rapid, and it has developed into one of the most popular furnaces. The furnace is designed for rapid melting and can be interchangeably arranged for either



FIG. 178. A 100-ton Heroult furnace, 20,000 kv-a., 20 ft. by 29 ft. inside of shell, six 18-in. electrodes. Average charge about 95 gross tons, maximum charge 135 gross tons. (*Courtesy American Bridge Company.*)

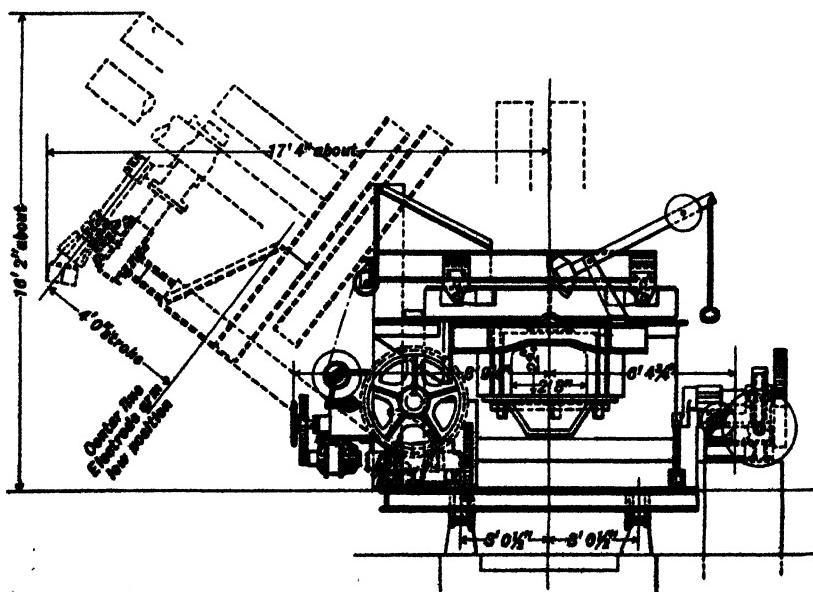


FIG. 179. A Heroult furnace with tilting top for charging. (*Courtesy American Bridge Company.*)

acid or basic melting. Three vertically adjustable electrodes are arranged in triangular formation and enter vertically through the spheroidal roof. The furnace operates on a three-phase star-connected secondary, neutral-connected circuit as shown in Fig. 165d. It tilts in two directions, backwards toward the charging door for slagging and forward with the tapping spout for pouring. It is arranged to tilt on

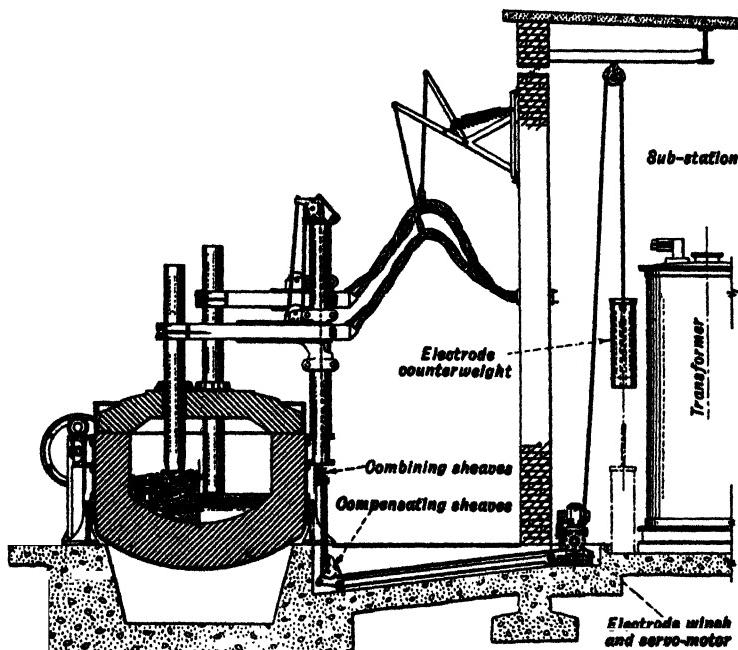


FIG. 180. Schematic cross-sectional view of an installation of a Moore Rapid Lectromelt furnace.

rockers so designed as to cause the spout stream when tapping to move in a substantially vertical direction, avoiding the necessity for racking the crane to keep the ladle under the stream. The furnace has a thermal efficiency above 75 per cent during the melting process. When it is used on cold scrap with no refining the energy consumption is 458 kw-hr. per ton of charge; with basic melting and refining the energy consumption may be 600 kw-hr. or more per ton. Figure 180 shows a furnace in section with counterbalanced electrode arm and method of connecting it to the transformer. Figure 181 shows a commercial installation of a Lectromelt furnace.

A special lift-and-swing-aside roof has been developed for rapid charging from drop-bottom buckets. Compared to door-charge furnaces

this method of charging shows considerable saving in man-hours and in the life of the electrodes and refractories.

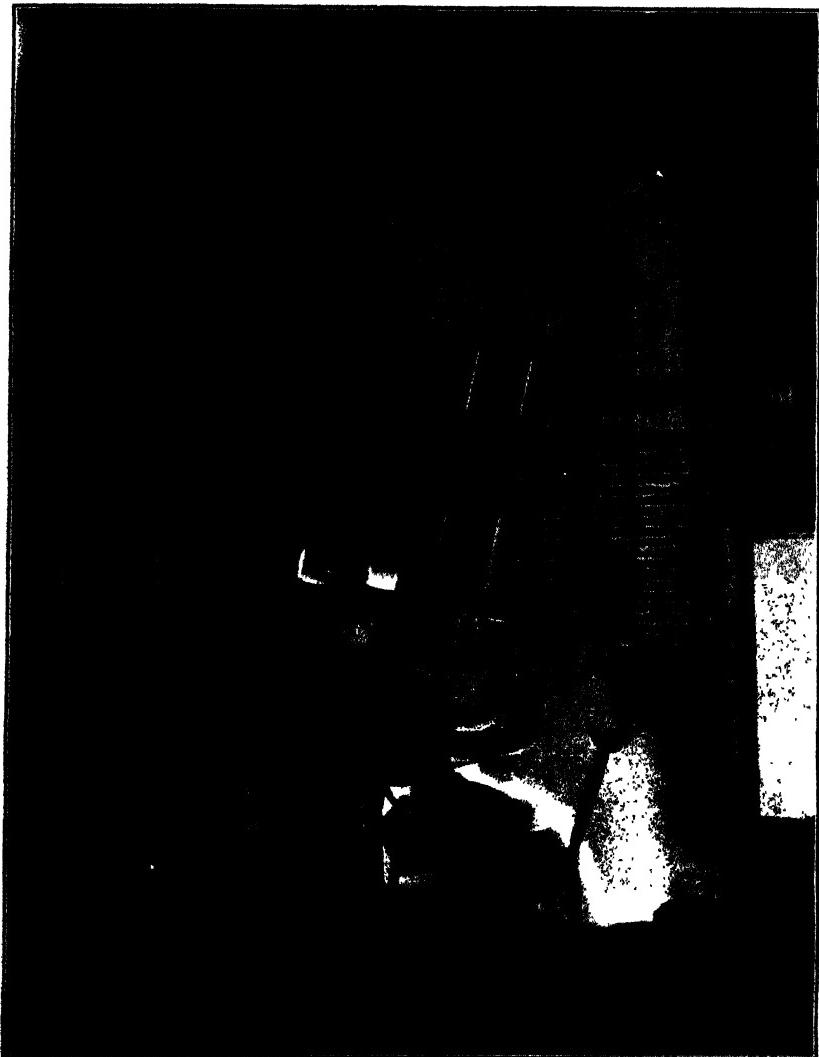


FIG. 181. A one-ton per hour Lectromelt furnace. (*Courtesy Pittsburgh Lectromelt Furnace Corporation.*)

Other Series-Arc Furnaces. A number of other series-arc furnaces have been developed, some of which have features of special merit, but commercially they do not find the application that the Heroult and Lectromelt furnaces do.

The *Swindell* or *Brooke* furnace is a tilting series-arc furnace of simple and rugged construction. Three electrodes are arranged in triangular fashion. The electrode mast and supporting superstructure have been entirely removed from the furnace shell, thus simplifying the construction and adjustment and reducing electrode breakage. Special electrode economizers prevent the combustion of furnace gases that escape through the clearance in the electrode ports in the crown; these economizers save electrode oxidation and reduce wear on the roof refractories. No water cooling is necessary for the electrode clamps, but cooling rings in the roof and door arches are water cooled. Figure 165a, page 387, shows a Swindell furnace.

The manufacturers of the Swindell furnace supply a multiple melting system for continuous pouring of castings. Two furnaces are mounted on a rotating platform; the same transformer and set of electrodes are used for each furnace alternately. One furnace is melting while the other is pouring a finished heat. As in the single furnace, when the furnace is ready to pour a heat the electrodes are lifted rapidly out of the furnace and the turntable is turned half a revolution. While one furnace is pouring, the other is being charged and then melts. The time-lapse between shutting off the power on one furnace and turning it on for the other is less than 3 minutes.

The *Fiat* furnace, developed in Italy, is a modification of the three-phase, three-electrode direct series-arc furnace. The hearth is slightly conductive and is connected to the center point of the star transformer connection on the secondary side and is grounded so that, under balanced load, little current flows to the ground. Installations up to the present have been limited to plants in Europe.

The *Volta* furnace, developed in Canada, is a modification of the Heroult; it is of three-phase, three-electrode direct series-arc type.

The *Vom Baur* furnace⁸ is oval in shape and has three carbon electrodes arranged in line. The central electrode acts as a common return and, therefore, carries more current than either of the other two electrodes. The *Ludlum* furnace, like the Vom Baur, is oval, has its three electrodes in line, and operates on three-phase current. It has a door at each end of the large axis and may be tilted toward each door for pouring. Current at 90 to 100 volts is used. A 10-ton furnace uses 12-in.-diameter graphite electrodes and consumes about 2,250 kv-a. The furnace is used successfully for steel melting and for the duplexing of gray iron for castings. The metal is melted in a cupola and is then transferred to the

⁸ C. H. Vom Baur, *Trans. Am. Electrochem. Soc.*, 23, 237 (1918); and *Chem. & Met. Eng.*, 20, 488 (1919).

electric furnace for superheating, desulphurizing, and freeing the metal from slags, oxides, and dissolved gases. The *Greene* furnace, like the Ludlum and Vom Baur, has three electrodes in line, but it is built in a cylindrical shell which rolls forward for pouring. The shell rests on two rails and is tilted by means of hydraulic cylinders located behind the shell. The circular construction permits a higher roof and longer arcs. The furnace operates on 130 to 150 volts. The *Booth* furnace also has three electrodes in line and is oval in shape. The standards supporting the electrode holders are located at the side of the furnace which tilts on end. The furnace is built on two rockers, each of which rests on two rollers. A curved rack is attached to one of the rockers. A pinion driven by a worm gear engages the rack and is operated by an electric motor with push-button control.

The *Stobie* furnace has found considerable application in Great Britain but not in the United States. Electrode economizers seal the electrodes in the roof so that heat is not lost on account of escaping flames, and air, which oxidizes the electrodes, cannot enter the furnace. Furnaces with capacities from 6 to 25 tons have four electrodes in line; those with greater capacities have six electrodes in line and use three-phase current, each phase with its own return. The *Arnold* furnace is of the Heroult type and is built in small sizes only. A furnace with a 1,000-lb.-per-hr. rating has a 5-ft.-diameter shell and an average charging capacity of 2,500 lb. and a maximum of 4,000 lb. with a 500-kv-a. transformer capacity. A 2,000-lb.-per-hr.-rating furnace has an average charging capacity of 4,000 lb., a maximum of 5,500 lb., and a 800-kv-a. transformer capacity. The Arnold furnace has found application in shops for experimental purposes, and during periods of small demand it is exceptionally suited for "bleeder" service; i.e., it is connected to the transformers and switchboard of a larger furnace, so that instead of operating a large furnace for perhaps a few hours a week, which creates a relatively high demand charge, the smaller furnace is operated over a longer period of time at a lower demand.

The furnaces described in this section are of the direct series-arc type in which the arc forms between the electrode and the furnace charge. The current passes from an electrode to the charge and back to another electrode. They are represented in America chiefly by the Heroult, Lectromelt, Ludlum, and Volta furnaces. The furnaces described in the next section are also direct-arc furnaces, but an electrode is placed in the hearth so that it makes direct contact with the charge. The current forms an arc as it passes from the electrode to the charge; it then passes through the charge and out the bottom electrode.

Hearth-Electrode Furnaces

The *Girod* furnace introduced in about 1905 was the earliest example of the hearth-electrode furnace. It has found successful application in Europe, but there are only isolated installations in this country. It is a tilting furnace generally square in plan as shown in Fig. 182. Four electrodes pass through the roof of the three-phase furnace. The single-phase furnace formerly used has but one top electrode. The bottom electrode consists generally of 16 soft-steel bars imbedded in the refractory hearth, each one being water cooled at the bottom end. The upper part of each rod becomes melted, but frozen metal at the end of the heat keeps them built up.

The arcs are in parallel; the voltage is about half that of a Heroult whereas the current is double that for furnaces of equal load. A 15-ton furnace requires about 65 volts. The Girod is used chiefly on cold scrap, and one of its advantages is the steady load on cold scrap due to the even flow of the current to and from the bottom electrode. Heating is by resistance as well as by the arc.

The *Keller* furnace works on the same principle as the Girod; the bottom consists of an iron plate to which are attached a number of iron rods placed vertically upwards. The rods are about 1 in. in diameter and 2 ft. long. The space between the bars is filled with burnt dolomite or magnesite and tar rammed in place to form the hearth. Small furnaces are of the single-phase type as shown in Fig. 166b, page 387. Larger ones use three electrodes, three-phase with no current flowing through the hearth when phase loads are in balance. The Keller furnace has not found favor in the United States but is in use in Continental Europe.

The *Snyder* furnace came into the field in 1910 as a direct competitor of the Heroult. Snyder, however, used a single top electrode with a

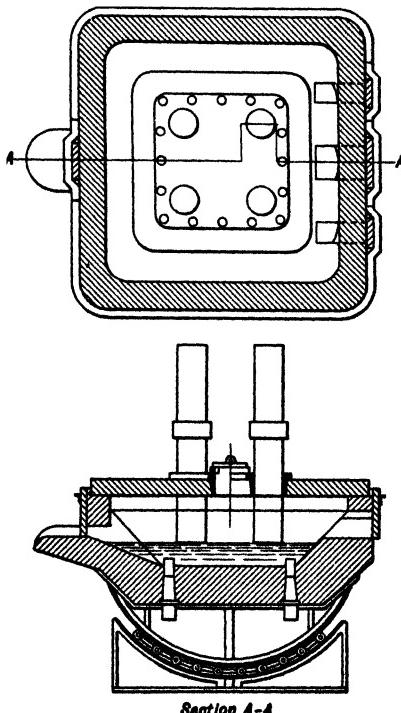


FIG. 182. Section through a 10-ton Girod furnace.

water-cooled electrode built into the furnace bottom. Since the furnace had only a single vertical electrode it could be placed in the geometrical center of the cylindrical furnace crucible, so that there was little tendency for the arc to blow or lap the side walls. The Snyder furnaces utilized relatively high voltages of 110 to 220 volts, depending upon the size of the furnace, whereas the Heroult usually has 80 to 120 volts across the electrodes. Small graphite electrodes were used with a long arc. To protect the roof refractories the furnace shells were made relatively high and were equipped with tight-fitting doors. During the first World War Snyder became impressed with the necessity of saving time on furnaces, as electric furnaces were becoming larger in size, and time consumed became an objectionable and expensive feature in their operation, some large furnaces requiring more than an hour for charging.⁹ Accordingly he devised a simple pivot for pulling back the roof by the same mechanism that tilted the furnace forward for tapping. With the roof and the electrodes out of the way the furnace crucible could be charged through the top with a drop-bottom bucket.

Units larger than 5 tons were later built to operate on three-phase, one phase connected to the hearth electrode, the other two to two vertical electrodes in the roof.

The *Lectrosimplex* furnace is a small single-phase furnace built in capacities from 50 to 200 lb. It is especially suited for handling relatively small outputs. The various sizes will melt their normal charges of cold steel scrap in about 80 minutes. The standard construction consists of one top electrode, the current passing through the charge and out the bottom, but two-top-electrode single-phase construction is available; by proper changes in construction the furnace may be altered to three-phase.

Conducting-Hearth Furnaces

In conducting-hearth furnaces, the refractory hearth becomes conducting, especially at elevated temperatures. No special conductor or electrode passes through the hearth, but usually care is employed in placing a good conductor in contact with the refractory, and as a result this type of furnace is also called a buried hearth-electrode furnace. Actually the whole hearth refractory is the electrode, and in order to obtain good electrical contact, a large copper plate is placed at the bottom of the furnace, with the refractory resting on the plate, or steel conductors are imbedded in the lower part of the hearth.

⁹ W. E. Moore, "Twenty Year Advance in Electric Arc Furnaces for the Production of Iron and Steel," *Trans. Am. Electrochem. Soc.*, 60, 65-85 (1931).

The *Grönwall-Dixon* furnace, called the *Electrometals* in Great Britain, is built with a hearth that has very little electrical resistance. The hearth is built up of dolomite and a bonding material rich in graphite. A $7\frac{1}{2}$ -ton furnace employs 12-in.-diameter electrodes taking a maximum power input of about 13,000 kw. It takes a current of about 18,000 amp. at 90 volts. The Electrometals furnace finds its widest use in England.

The *Greaves-Etchells* furnace, in contrast to the highly conducting hearth of the Grönwall-Dixon, has a high-resistance hearth, so that the hearth is heated by the current. A heavy copper plate rests on the bottom of the furnace shell under the hearth refractory as shown in Fig. 183. On top of this copper plate is a layer of graphite mixed with tar, and above this a layer of amorphous carbon. On top of the carbon is a layer of magnesite or a mixture of magnesite, dolomite, and hot tar. Each layer is rammed solidly in place. The tarry materials distil off in the first heating.

The hot refractories of the hearth cause convection currents to form in the molten charge. This prevents localized overheating and causes thorough mixing of the charge. This is especially valuable in the manufacture of alloy steel where the heavier alloying metal tends to settle to the bottom. It is also of value in refining, for the metal in contact with the slag is constantly changing. It is claimed by some, however, that these convection currents disturb the quiet dead-melted condition desirable toward the end of refining for elimination of solid impurities in the melt.

Mixed Types of Furnaces

The *Booth-Hall* furnace¹⁰ is equipped with one, two, or three roof electrodes corresponding to the number of phases in the power supply. The hearth contains buried conductors and becomes conducting at high temperatures. With single-phase and two-phase power the whole current passes through the conducting hearth during the refining period and

¹⁰ W. K. Booth, *Trans. Am. Electrochem. Soc.*, 33, 247 (1918); *Met. Chem. Eng.*, 18, 211 (1918).

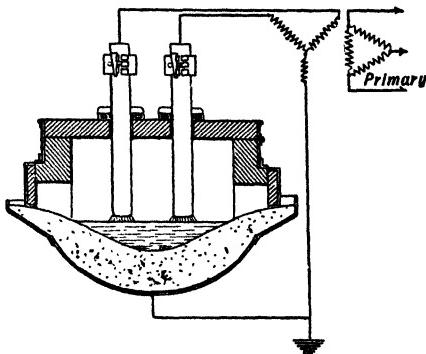


FIG. 183. Section through a Greaves-Etchells furnace, conducting-hearth type. Two phase through top electrodes, one phase through bottom.

considerable heat is generated in the hearth. With three-phase supply, the hearth acts as the neutral point and carries current only when the phase loads become unbalanced.

An auxiliary electrode is provided through the roof which is connected in parallel with the hearth. When melting cold scrap, before the hearth has become hot enough to carry any appreciable current, the auxiliary electrode rests with its weight directly on the charge. The whole of the return current passes through it at the start. After 15 to 45 minutes' operation, depending on the heat in the furnace when charged, the hearth becomes sufficiently conducting and the auxiliary electrode is withdrawn. Furnaces have been built up to 15-ton capacity, but a 4- to 5-ton furnace is more common.

The *Nathusius* furnace¹¹ is of German origin. The three phases of a star-connected secondary lead to the carbon electrodes through the roof; three conductors buried in the hearth are connected to their separate returns. The metal bath acts as the neutral point of the transformer, current passing to it from the upper carbon electrodes and the steel conductors in the hearth.

In the *Tagliaferri* furnace are combined the principles of independent-arc heating with direct series-arc heating. Three-phase low-voltage current is general practice, but two-phase has also been used successfully. The three-phase furnace has three roof electrodes and three electrodes entering almost horizontally through the side of the furnace, as shown in Fig. 168a, page 388. During the melting period arcs form between the roof electrodes and the corresponding side electrodes. It is claimed that this insures a greater steadiness of load and more even distribution of heat during melting. During the refining period the furnace is operated with direct-arc heating in order to obtain high slag temperatures.

Induction Furnaces

Induction furnaces have not found extensive application in ferrous metallurgy in the United States, except that the Ajax-Northrup high-frequency furnace and the Ajax-Wyatt are gradually being adopted in this field. In Europe, induction furnaces find wider application in ferrous metallurgy. The fundamental principles have been discussed, beginning on page 389.

The development of induction furnaces cannot be attributed to any one person. E. A. Colby in the United States, Ferranti in England, and Kjellin in Sweden independently developed induction furnaces. Kjellin's was the first to find practical application in steel melting in 1910.

¹¹ W. Lipin, *Met. Chem. Eng.*, 10, 227 (1912).

Kjellin Furnace. The Kjellin furnace is shown diagrammatically in Fig. 184. It has a primary made of insulated copper wire, air cooled, or in some designs is made of water-cooled copper tubing. The core is built up of laminated sheets of soft iron. The steel charge, contained in a ring-shaped refractory-lined annular channel, forms the secondary. The furnace cannot be started on cold scrap. In starting a cold furnace,

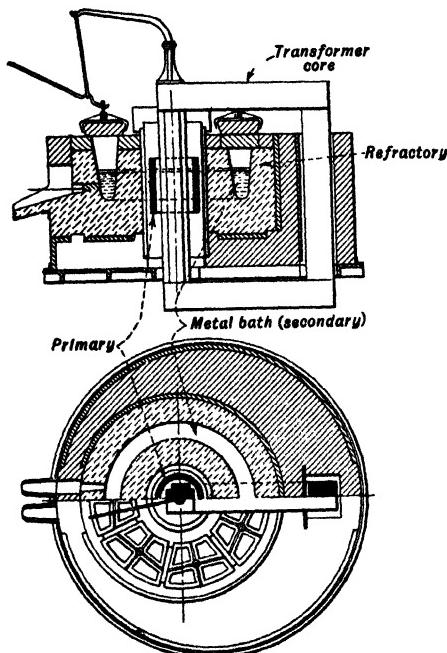


FIG. 184. Kjellin induction furnace.

either a steel ring must be placed in the channel or a charge of molten metal must be supplied to the furnace. When a furnace is in continuous operation some of the molten material is left in it after pouring, so that currents can pass after recharging. Therefore two tap holes are supplied, one for complete draining of the hearth, and one placed a little higher for partial draining. The furnaces are built in fixed and tilting types and in sizes up to $8\frac{1}{2}$ -ton capacity. A 2-ton furnace operates on 3,000 volts in the primary and 30,000 amp. in the secondary, and consumes 750 to 850 kw-hr. per ton of steel, using cold pig and scrap. In order to keep the power factor up to a reasonable amount, low frequencies of 5 cycles per second alternating current are used.

Röchling-Rodenhauser Furnace. This furnace, shown diagrammatically in Fig. 185, has a secondary in the shape of a figure 8, or it may have

three channels connected to the central hearth. It was designed to eliminate the small capacity and low power factor in the Kjellin furnace

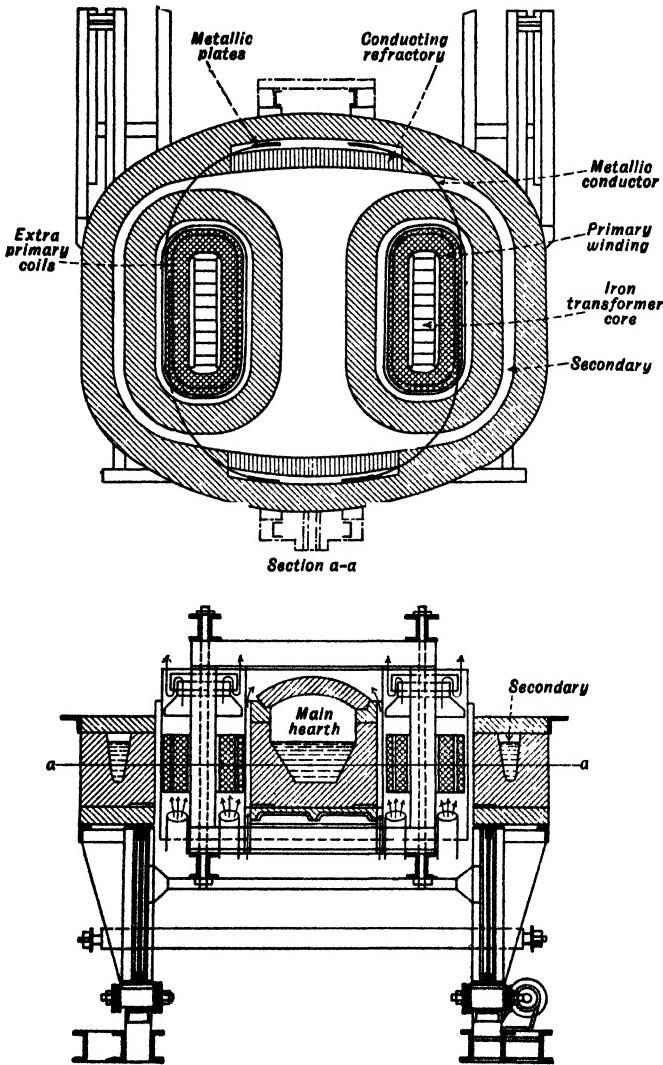


FIG. 185. The Röchling-Rodenhauser induction furnace.

by the application of a combination induction and resistance principle. In addition, the large central hearth simplifies slagging operations. In order to heat the central hearth, auxiliary secondary windings consisting of a few turns of strip copper are provided, separated from the primaries by a small air gap only, and connected electrically to the hearth elec-

trodes or pole-plates at the opposite ends of the hearth as shown in Fig. 185. These pole-plates consist of plates of steel imbedded in the furnace wall and coated with calcined dolomite. These oxide layers become conducting at high furnace temperatures and extra current passes through the steel in the central hearth. The hearth is thus kept at high temperatures, permitting the use of refractory slags.

Single-phase furnaces have been built with a capacity of $8\frac{1}{2}$ tons consuming 700 to 740 kw. with primary voltage of 4,000 to 5,000 volts.¹² The furnace operates with a power factor of 0.7 to 0.8 at a frequency of 25 cycles. When it is charged with molten Bessemer steel the power consumption is 120 to 160 kw-hr. per ton of steel; with cold scrap it is about 900-kw-hr. per ton.

Other Induction Furnaces. Several other induction furnaces have been developed for use in steel refining. A 2-ton furnace designed by the General Electric Company for use at its Pittsfield, Massachusetts, plant¹³ consumes 250 kw. The primary takes a 15-cycle, single-phase current at 2,200 volts.

The Ajax-Northrup high-frequency furnace is finding extended use in steel refining, but its chief application has been brass melting; it is discussed under non-ferrous melting on page 426.

The Ajax-Wyatt low-frequency furnace is applicable in duplexing cast iron, but it too finds its chief use in non-ferrous metallurgy and is discussed under the same heading as the Ajax-Northrup furnace.

OTHER APPLICATIONS OF ELECTRIC FURNACES IN FERROUS METALLURGY

In the preceding pages the application of electric furnaces in steel refining was discussed. But in addition to steel refining and to a small amount of ore reduction, electric furnaces find application in other phases of ferrous metallurgy.

"Synthetic" Cast Iron. During the first World War synthetic cast iron was made in France, Germany, Canada, and northwestern United States, where steel scrap was comparatively cheap and cast-iron scrap and pig iron expensive. In one method scrap borings and turnings were melted in a basic electric arc furnace. The melt was brought to 1,350 to 1,450° C. (2,462 to 2,642° F.) and was then carburized to 3.50 per cent carbon by the addition of petroleum coke, electrode stubs, charcoal, or low-ash bituminous coke. Ferroalloys were added to supply the

¹² A. J. Allmand and H. J. T. Ellingham, *The Principles of Applied Electrochemistry*, second edition, p. 589, Edward Arnold and Company, London, 1924.

¹³ *Iron Age*, 108, 344 (1921).

required silicon and manganese, and the metal was cast directly into molds, or into pigs, if it was to be sold. After the close of the war the method did not find much favor.

Gray and Malleable Cast Iron. The stricter specifications for gray and malleable cast iron have in a number of cases led to a duplex process, in which an electric arc or induction furnace supplements a cupola. A cupola offers no opportunity to remove the sulphur or reduce the phosphorus in the pig-iron charge. The cost of this duplex process is greater, but the saving in decreased defective castings and increased quality are said to offset the added cost.

The iron is melted in a cupola and is then transferred to a basic electric furnace to be desulphurized, deoxidized, and degasified. Conditions are so maintained that the silicon and carbon contents are not reduced. White and carbide slags are used as mentioned under steel refining, but the furnace temperature need not be as high as in steel furnace, though it is higher than in the cupola so that casting is greatly facilitated.

ELECTRIC FURNACES USED MAINLY FOR NON-FERROUS METAL MELTING

Electric furnaces found their first commercial application to brass and bronze melting in about 1916; since then their application in this field has grown rapidly so that today probably more than 95 per cent of all brass melting in the United States is done in electric furnaces. The furnace temperatures required for brass and bronze melting are lower than those in steel practice, and, owing to the volatility of the zinc in brasses, direct-arc furnaces have not found extensive application in this field. In current practice, brass melting is largely carried out in an indirect-arc furnace, the Detroit rocking furnace, and in two types of induction furnaces, the Ajax-Northrup and the Ajax-Wyatt furnaces. In addition, the Booth rotating-arc furnace has in the past found considerable application in brass melting, and the Bailey furnace with a granular carbon resistor also once enjoyed popularity, but in the United States at least, they have had to give up a good share of the field to the other furnaces. The Rennerfelt furnace, with its indirect arc, has found application in Europe for non-ferrous melting. In this country, however, furnaces like the Detroit, the Ajax-Wyatt, and the Ajax-Northrup, once used almost exclusively for non-ferrous melting, are gradually finding application in iron and steel metallurgy also.

Electric furnaces have found wide favor in non-ferrous melting because the temperature can be held uniformly at the desired point, and oxidation and volatilization losses can be greatly reduced.

Detroit Arc Furnace. The Detroit furnace¹⁴ is built up of a cylindrical steel shell as shown in Fig. 164d, page 386, and Fig. 186, lined with refractories. Two electrodes project horizontally into the furnace from the ends of the cylinder. The furnace is mounted on rollers and during operation is rocked backward and forward automatically by an electric motor. The graphite electrodes are connected to the transformer through flexible leads. The distance between the electrodes is varied



FIG. 186. A 500-lb. Detroit rocking furnace. (Courtesy Detroit Electric Furnace Corporation.)

manually, and this method can be used to regulate the power input into the furnace. During charging, the electrodes are withdrawn for protection until their inner ends are flush with the furnace walls. Rocking of the furnace is begun as soon as superficial melting of the charge has started. At the start the angle of rotation is 80°; this is gradually increased to 200° by the time the charge is melted. This rocking avoids superheating of the lining and insures a very uniform product in any one heat. A combined door and spout is used for charging and tapping the furnace.

Furnace sizes vary from 250- to 300-lb. charging capacity, with power input of 75- to 350-kv-a., single-phase, 60-cycle current. Heats are

¹⁴ A. E. Rhoads and C. H. Morken, *Trans. Am. Electrochem. Soc.*, 61, 161 (1932); and E. L. Crosby, *Elec. Eng.*, 53, 132 (1934).

turned out in 15 to 60 minutes, depending upon the furnace size and the need of haste. Power factors of 75 to 85 per cent are generally maintained.

The Detroit furnace serves for a variety of purposes. In addition to its large field of non-ferrous metal melting it is used for producing high-alloy irons, gray iron, and stainless steels. It is used for glass melting for development and semi-production work. The furnace is supplied with air ports for the introduction of air or other gases for maintaining any desired degree of oxidation or reduction within the furnace.

The furnace is also used for the production of strontium oxide and for the smelting of cobalt ores.

Ajax-Wyatt Low-Frequency Induction Furnace. The Ajax-Wyatt furnace operates on the transformer principle; the secondary consists of a vertical loop of the molten metal contained in a refractory channel. The bulk of the metal is above this secondary as shown diagrammatically in Fig. 187. This metal exerts a static head on the liquid metal in the secondary and thereby overcomes the "pinch" effect which is troublesome in horizontal-channel furnaces as explained on page 390.

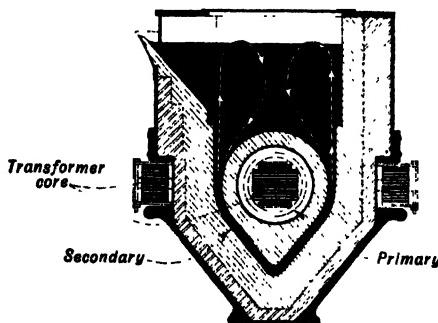


FIG. 187. Sectional view of an Ajax-Wyatt induction furnace.

The heating of the metal takes place in the V channel where a relatively large current flowing through the metal generates heat at a constant rate, by reason of the resistance of the metal. The hot metal rises, and cooler metal from the main chamber takes its place. Stirring action is also produced by the motor effect. The agitation produced is clearly shown in Fig. 188.

More than 5,000 Ajax-Wyatt furnaces are now installed throughout the world, and according to the manufacturer's literature over 93 per cent of all wrought brass manufactured in America is melted in Ajax-Wyatt furnaces.

The furnaces are built in standard sizes ranging from 200- to 3,000-lb. capacities, with power inputs of 30 to 240 kw. They operate on 25, 30, or 60 cycles alternating current on any commercial voltages, such as 220, 440, or 550 volts, single-phase, except that the 2,000- to 3,000-lb. size uses three-phase current.



FIG. 188. View of the metal bath in an Ajax-Wyatt furnace. (*Courtesy Ajax Electric Furnace Corporation.*)

When a heat is poured, sufficient molten metal is left in the furnace to complete the vertical ring, unless the furnace is to be cut out of service, when all the metal is removed. In starting a cold furnace, sufficient molten metal is first poured into the furnace to complete the circuit in the vertical ring. If a foundry shuts down for the night a low power supply may be left connected to the furnace to just keep the metal in the channel molten.

The furnaces can be used for melting most non-ferrous alloys, such as red brass valve mixtures, yellow and red brass plumbing fittings, hardware alloys, ornamental bronzes, nickel-silver, phosphor bronze, copper, zinc, and zinc-base alloys. The furnaces, with special design, have

been used for dipbrazing bicycle frames. A more recent use has been in connection with the continuous duplexing process for cast iron. The iron is melted in an ordinary cupola, and the liquid metal is then transferred to the induction furnace, which serves as a forehearth. Here the alloy additions are made and the metal is superheated to any desired degree, after which the cast iron is tapped at regular intervals.

The only maintenance cost is that of the refractory linings, which show a life of 1,000 to 15,000 heats. The kilowatt-hour consumption per ton of metal varies according to the nature of the metal or alloy. For zinc it is 90, for copper 310, kw-hr. per ton of metal at the pouring temperature. The power consumption for brasses and bronzes lies between these figures. The average metal loss is less than 0.5 per cent. The power factor varies between 0.7 and 0.8 on 60-cycle current supply.

Ajax-Northrup High-Frequency Induction Furnace.¹⁵ The high-frequency induction furnace, in contrast to the other types of induction furnaces discussed, has no transformer core. The furnace consists of a helical inductor coil or primary winding and a cylindrical refractory crucible located concentrically inside the inductor coil. When supplied with electric power at a relatively high frequency the furnace will easily melt a charge of cold scrap of any size.

The principle of the high-frequency induction furnace cannot readily be stated in simple non-mathematical terms. The authors referred to have presented a theory in as simple terms as the nature of the problem will permit, and it will not be repeated here, except to state that, when an alternating current flows through a metal conductor, the current density over a section of the conductor is not uniform. In an isolated conductor the highest current density is obtained at the surface, according to the laws of electromagnetic induction. If the frequency of the current and the permeability of the conductor are relatively high, and the resistivity relatively low, practically all the current will be confined to a thin surface layer or skin. The problem can be handled by assuming that the induced current in the conductor is distributed uniformly over a definite skin depth. This depth can be calculated by the formula

$$T = \frac{1}{2\pi} \sqrt{\frac{\rho}{\mu f}}$$

T = centimeters

ρ = resistivity of the conductor in absolute cgs units

μ = magnetic permeability

f = frequency, cycles per second

¹⁵ Considerable information has been published on high-frequency induction furnaces. A general article covering both theory and practice is that of C. A. Adams, J. C. Hodge, and H. M. Machusick, *Elec. Eng.*, 53, 194 (1934). This article gives a selected bibliography.

For steel the above authors assume ρ to be 200 microhm-cm., and μ to be unity. With a given current frequency available, the authors then show how to calculate the volts per turn in the primary, from which the necessary number of turns can be computed according to the supply voltage.

It is necessary to have a supply of high-frequency current; 1,000 cycles per second has become almost standard for commercial-size furnaces. This is supplied by a single-phase alternator usually driven by a polyphase synchronous motor. The power factor for this type of furnace is inherently low, in some cases not above 0.1. The cost of a high-frequency alternator to supply such a furnace direct would be pro-

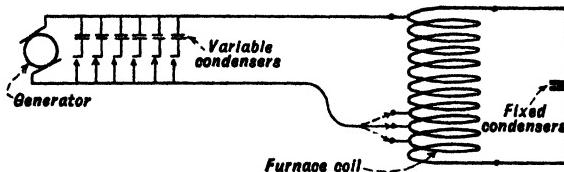


FIG. 189. Basic wiring diagram of an Ajax-Northrup furnace and converter, motor-generator type;

hibitive. Consequently capacitors are used to supply the large quadrature lagging current required by the furnace. Therefore, the generating or supply equipment for commercial sizes consists ordinarily of a single-phase high-frequency alternator driven by a polyphase synchronous motor with a bank of capacitors adjustable by relatively small steps and connected in parallel as shown diagrammatically in Fig. 189. The power factor is about 0.6 on average loads.

For laboratory-size furnaces, much higher frequencies than 1,000 cycles per second are obtained with the aid of mercury gap oscillators. Frequencies of 15,000 to 45,000 cycles per second are general for this type of equipment. A simplified diagram of a circuit of this type is shown in Fig. 190. In addition, small furnace units have been made using an electronic rectifier and inverted tubes for the generation of high-frequency currents, but as yet this method has not found commercial application.

Most commercial units take voltages of the order of magnitude of 1,000 volts, although 2,000 volts have been applied. Higher voltages decrease copper losses and permit the use of smaller bus-bars and connectors, but the necessity for some exposed conductors and the limitation in the insulation of the furnace coil preclude very high voltages.

High-frequency induction furnaces possess the advantages of other types of induction furnaces, such as carbon-free melting, excellent mixing,

high efficiency, good load characteristics, close control, and comfortable working conditions. In addition they will start readily on cold scrap, and they have a high melting rate. For instance, in commercial practice, 250 lb. nickel-iron has been melted in 22 minutes. Figure 191 presents a sectional view of a furnace showing stirring of the molten charge and the magnetic field.

High-frequency induction furnaces have a wide variety of uses. For metal melting, the furnaces are used for production melting of steel, tool

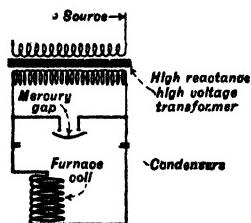


FIG. 190. Basic wiring diagram of an Ajax-Northrup furnace and converter, mercury gap type.

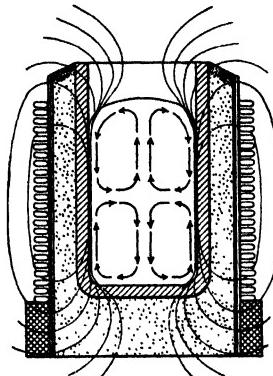


FIG. 191. Sectional view of an Ajax-Northrup furnace showing circulation of molten charge and magnetic field.

steel, stainless steel, iron, bronzes, nickel-silver, precious metals, and a variety of alloys. In all such cases the secondary current is generated in the metal charge itself. Furnaces are built ranging in capacities from 100 to 2,200 lb. Figure 192 shows an Ajax-Northrup furnace containing 4 tons of steel.

Units are also built for heat treating and forging; parts of forgings can be heated to the desired temperature while the remainder of the piece stays cold.

Non-conducting materials are heated in a special graphite crucible placed in the furnace, the heat being generated by the induced current in the crucible walls, and temperatures above 3,000° C. (5,432° F.) can be obtained. In this way refractory materials, clays, and glass can be heated. Figure 193 shows a furnace especially adapted for determining the fusion point, more properly called the pyrometric cone equivalent, of refractory materials. The energy absorber is a sleeve constructed of Acheson graphite machined from an electrode. The sleeve is fitted with a graphite cover and a 6-in. extension tube which serves as

a peep-hole and for taking temperatures with an optical pyrometer. An opening at the bottom serves as an entrance for air when oxidizing



FIG. 192. An Ajax-Northrup induction furnace holding 4 tons of steel. (Courtesy Ajax Electrothermic Corporation.)

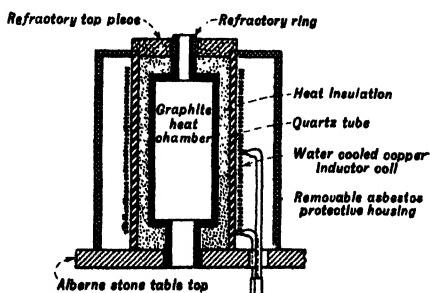


FIG. 193. Graphite lined Ajax-Northrup furnace for testing refractories.

conditions are desired. The sleeve is usually lined with a highly refractory lining such as zirconia or magnesia when oxidizing conditions must be maintained.

Russ Induction Furnace. The Russ furnace has been in use for non-ferrous melting in Europe for a number of years. The furnace is of the hearth type¹⁶ and is built in larger units than the American furnaces.

A 3,500-lb. furnace melts a charge of brass in an hour with a power consumption of 170 kw-hr. per ton of brass. The furnace is also used for the continuous electric annealing of brass strips. A sectional view of the Russ furnace is shown in Fig. 194.

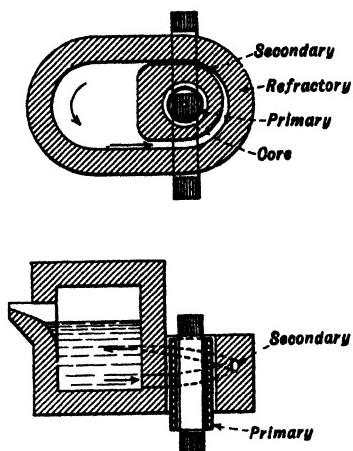


FIG. 194. Russ induction furnace.

Surrounding the hearth and raised above was an annular refractory channel filled with granular carbon or graphite which served as the resistor. The refractory channel was made of Carborundum firesand. The granular resistor was ground to $\frac{1}{4}$ -in. mesh. Current was conducted to the resistor by heavy graphite electrodes entering the ring at opposite sides. The heat produced in the resistor was radiated from the trough, a large amount being reflected from the roof on to the bath.

The furnaces were built about 7 ft. in diameter and 6 ft. high. A furnace holding 1,500 lb. brass consumed 105 kw. at an average current of 100 volts and 110 amp., with a power factor of 0.98. The furnaces are no longer used for brass melting, but they have been found to possess certain advantages for the heat treating of metals.

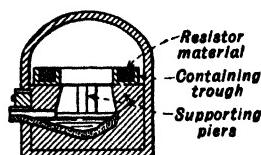


FIG. 195. Baily resistance furnace.

FERROALLOYS

A ferroalloy is an alloy of iron and one or more other metals. Ferroalloys are utilized in steel manufacture, a suitable alloy being added to

¹⁶ E. F. Russ, *Trans. Electrochem. Soc.*, **61**, 207 (1932).

¹⁷ T. F. Baily, *Chem. & Met. Eng.*, **21**, 11 (1919); *Trans. Am. Electrochem. Soc.*, **20**, 37 (1921).

the molten bath, generally at the end of the purification process. The purpose is to introduce into the steel certain proportions of the alloy metal to give the finished product definite physical properties. Ferroalloys are also used for recarburizing, and as cleansing and deoxidizing agents. In the last application the alloy metal combines with oxygen, oxides, or other impurities and then passes into the slag.

Electric furnaces have found favor in the manufacture of ferroalloys on account of the high temperatures obtainable. The alloying metal is

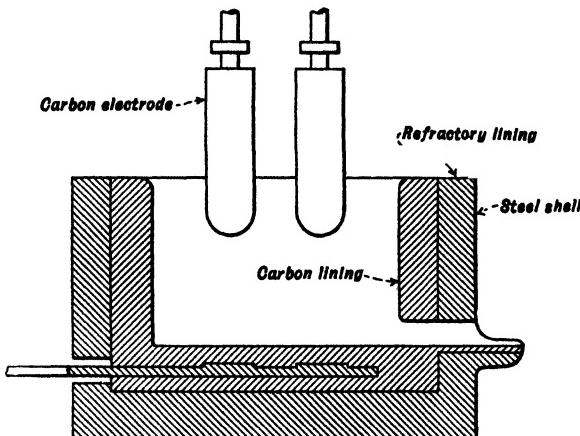


FIG. 196. General arrangement of a ferroalloy furnace.

not introduced into the furnace as a metal but as an ore, and some of these ores are quite refractory so that high temperatures are required for their reduction. Prior to 1899, when electric furnaces were first used in the United States for ferroalloy manufacture, the alloys were made in blast furnaces, and to some extent in open-hearth furnaces, but their manufacture was confined chiefly to 70 to 80 per cent ferromanganese, 10 to 12 per cent ferrosilicon, and 30 to 40 per cent ferrochrome. Even today much of the ferromanganese, ferrochrome, and ferrosilicon is made in blast furnaces, but grades containing more than 80 per cent manganese, 45 per cent chromium, or 20 per cent silicon are made in electric furnaces.

In Europe the overexpansion of the calcium carbide industry left many electric-arc furnaces idle, many of which were adapted to the manufacture of ferroalloys during the period when electric furnaces were being introduced for ferroalloy manufacture.

The furnaces used for ferroalloy manufacture are of simple construction, as shown diagrammatically in Fig. 196. They are single-, two- or three-phase, the simplest being the Siemens furnace which has a single

electrode suspended in the furnace from the top, the conducting hearth serving as the other electrode. The furnace shells are cylindrical or rectangular in plan, and a furnace may have a tap hole at its lower side, like ferrotungsten and ferromolybdenum furnaces. If the alloy formed cannot be tapped, the furnace can be partially taken down and the alloy button removed. Single-phase furnaces may also be built with two vertical electrodes, the current entering through one electrode and passing through the charge and out the other; but this type is little used. Three-phase furnaces for the production of ferrochrome, ferrovanadium, ferrosilicon, and ferromanganese have a rectangular or oval shell lined with refractory material, the bottom being lined with carbon. A tap hole is provided at the lower side. The furnaces have open tops to permit continuous charging, except that where volatilization losses may be great the furnaces are constructed with a roof.

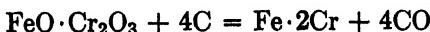
The furnace charge generally consists of metallic iron, such as turnings, or of iron ore and an oxidized ore of the alloying metal, and slightly more than the theoretical amount of carbon to reduce all the metals that are to be present in the alloy. The carbon may be anthracite coal, coke, or charcoal. The constituents of the charge are thoroughly mixed together and introduced into the furnace by shoveling or by mechanical devices. After part of the charge has been put into the furnace the suspended electrode or electrodes are lowered until they touch the charge, after which the remainder of the charge is added. A high-amperage current is then turned on, the carbonaceous material in the furnace charge carrying the current. Heat is produced largely by resistance heating, but there is also some arcing. When a high temperature is reached reduction takes place, and the reduced elements dissolving in each other collect in a pool in the bottom of the furnace. The alloy formed is saturated with carbon, the amount of carbon dissolved depending upon the nature of the alloy and the temperature attained. Ferrosilicon will hold 1 per cent or less of carbon; ferromanganese, 6 per cent or more. The tendency of the metals to volatilize may be reduced by piling up the charge and keeping it cool, or a roof may have to be built.

Ferrosilicon. On the basis of the amount produced, ferrosilicon is one of the most important ferroalloys. The iron may be introduced as steel turnings or as iron ore; the silicon, as lumps of ganister or quartzite or as sand; the carbon, as charcoal or coke. It is especially desirable that the iron ore or iron turnings and the coke be low in phosphorus and sulphur. The chief impurities in the raw materials are Al_2O_3 , CaO , and SiO_2 , but since the raw materials used are fairly pure, not much slag is formed. The slag boils up around the electrodes, where it is removed, as it is too viscous for tapping.

The furnaces have three vertical electrodes, and most of them operate on three-phase current. Heating is by resistance and arcing. The furnace shell is made of boiler plate lined first with a refractory lining and then with a carbonaceous layer. Part of the charge forms a crust along the lining and thus protects it. The furnaces are built with capacities of 4,000 to 12,000 kw-a., at 90 to 150 volts. The energy consumption ranges from 2 to 6 kw-hr. per lb., increasing with the silica content.

Ferrosilicon is used as a deoxidizer during steel refining when the steel is to be used for castings, for introducing silicon into cast iron, and for the production of high-silicon steel for electrical transformers. Steel with a silicon content of 4.75 per cent, known as "transformer steel," is considered the best material for magnet cores for alternating-current machinery. Ferrosilicon is also used for producing silicon iron, such as Duriron, for corrosion resistance.

Ferrochrome. Ferrochromium or, as it is known by steel men, ferrochrome, is made by reducing chromite with carbon in an electric furnace, according to the reaction



If pure materials are available no lime slag is necessary. Anthracite coal has been found to be a satisfactory reducing agent. The furnace product is an alloy containing 60 to 75 per cent chromium, 1 to 3 per cent silicon, and carbon up to 8 per cent. If the carbon content is kept below 4 per cent it is at the cost of increasing loss of chromium in the slag. Decarburizing was formerly accomplished by melting the alloy under a slag consisting of lime, chromite ore, and a little fluorspar, but at present the preferred method seems to be to use silicon or ferrosilicon high in silicon as the reducing agent.

The alloy is supplied to the trade graded as to carbon content, the classes being 4 to 5, 5 to 6, and 6 to 7 per cent carbon with the chromium content ranging from 65 to 70 per cent, and also as a low-carbon alloy ranging from 0.05 to 2 per cent carbon, and silicon content not above 1 per cent, the chromium content being 66 to 72 per cent. The melting points of these alloys range from 1,200 to 1,550° C. (2,192 to 2,822° F.).

Furnaces are of three-phase design with capacities of 2,000 to 5,000 kw. operating on 90 to 120 volts.

Ferrochrome is used for the production of chromium steels noted for their hardness, but it is not used very much by itself in alloy steels. Together with nickel and vanadium it is extensively used for armor plate, projectiles, gears, and high-speed tools and auto parts. It is widely employed in the production of heat-resisting chromium alloys and corrosion-resistant alloys. Stainless steel contains about 0.30 to 0.40 per

cent carbon and 12 to 18 per cent chromium. The alloy known as "18 : 8" contains 18 per cent chromium and 8 per cent nickel. For resistance to scaling at high temperatures, chromium steels contain 35 per cent chromium.

Ferrovanadium. The raw materials used for ferrovanadium production are vanadium ore concentrates high in vanadium oxide, V_2O_5 , smelted with iron and fluxes. Reducing agents may be coke, silicon, or ferrosilicon. Relatively high reduction temperatures are needed, and to avoid volatilization losses of the valuable metal the furnaces are closed at the top. To reduce volatilization losses further the furnaces are so constructed that the metals leave the electrode zone as soon as reduced or melted. Furnaces have capacities of 2,000 to 4,000 kw. and are built in single- and three-phase design. Voltages up to 250 volts are used.

Vanadium is one of the most powerful scavengers available for adding to liquid steel for the purpose of removing oxygen. Vanadium increases the hardness of steels so much that ordinary alloy steel is not made with more than 0.2 per cent vanadium in it, or the steel will become too brittle. So-called "super high-speed steel" contains about 2.25 per cent vanadium. Vanadium is not used much in binary steels, but in small amounts it improves the properties of other alloy steels, e.g., it is used in armor plate in conjunction with nickel and chromium.

Ferromolybdenum. Ferromolybdenum is produced from a molybdenum ore, such as molybdenite, MoS_2 , roasted and concentrated, or from the sulphide directly, iron or steel turnings, or scrap, with carbon or silicon as a reducing agent and lime as a flux. An alloy containing 50 to 60 per cent molybdenum is usually produced with carbon content ranging from 0.25 to 2 per cent. Ordinarily sulphur is under 0.25 per cent, silicon 1.50 per cent.

The furnaces used are single- and three-phase with capacities of 300 to 750 kw.

Ferromolybdenum is used for special steels where high strains are encountered as in certain aircraft and automotive parts. Calcium molybdate, $CaMoO_4$, containing 40 per cent molybdenum and 25 per cent CaO , is used for the production of ferromolybdenum.

Ferrotungsten. The raw materials for ferrotungsten production are tungsten minerals such as wolframite, $(Fe,Mn)WO_4$, or scheelite, $CaWO_4$, carbon or coal, iron ore or iron scrap, and a slag. The furnaces are single-phase, ranging in capacities of 500 to 750 kw.; they are dismantled at the end of a run and the solid piece of alloy removed. The alloy commonly contains 78 to 84 per cent tungsten, with carbon and

silicon not above 1.00 and 0.75 per cent, respectively. The melting point is between 1,800 and 1,900° C. (3,272 and 3,452° F.).

Ferrotungsten is used for high-speed tool steels and similar alloy steels. Self-hardening steels, such as Mushet steel, contain 4 to 12 per cent tungsten together with 2 to 4 per cent manganese and 1.50 to 2.50 per cent carbon. High-speed tool steels contain 14 to 20 per cent tungsten and will hold their edges at a red heat.



FIG. 197. A ferromanganese furnace. (*Courtesy Anaconda Copper Mining Company.*)

Ferromanganese. Ferromanganese is employed as a deoxidizer and as an alloying agent in the production of special steels. Steels containing 12 to 14 per cent manganese are very hard and tough. Manganese is also used to the extent of 1 to 2 per cent in engineering steels. Spiegel-eisen containing up to 20 per cent manganese and ferromanganese containing up to 80 per cent manganese were made in blast furnaces for many years.

Spiegeleisen used in Bessemer and basic open-hearth practice has a chemical composition of approximately 15 to 30 per cent manganese, 4.5 to 5 per cent carbon, a maximum of 1.00 per cent silicon, sulphur 0.05 or less, and phosphorus 0.15 or less. A standard grade of ferromanganese contains approximately 78 to 82 per cent manganese, iron 15 to 20, carbon 6 to 8, silicon 1.00 or less, phosphorus 0.35 or less, and

sulphur 0.05 or less. If used for low-carbon steels the ferromanganese should contain a maximum of 1 per cent carbon.

Ferromanganese furnaces are in general constructed similarly to the ferrosilicon furnaces, but are also built with closed tops with provisions made for the collection and utilization of the gaseous products from the furnace. The raw materials are manganese ores containing 45 to 50 per cent manganese, carbonaceous reducing agents, iron or iron ore, and in some cases a slag-forming agent. Smaller amounts of flux are used in electric than in blast furnaces, and usually the manganese recovery from the ore is greater, being 90 per cent or above.

The furnaces are of the arc resistance type, three phase, with capacities up to 9,000 kw. using 90 to 110 volts. An installation of a ferr manganese furnace is shown in Fig. 197.

REDUCTION OF NON-FERROUS METALS

Chromium. Little information is available regarding reduction of chromium ores, except that the chromium ore is reduced with silicon in an electric furnace. Chromium metal is not prepared in large amounts for in many cases where chromium is desired it may be introduced as ferrochrome. In electroplating of chromium no chromium anodes are used. (See under chromium plating.)

A special furnace has been developed for the reduction of chromium ores. The furnace is of the horizontal-electrode indirect-arc type similar to the one shown in Fig. 164a, page 386. The electrodes are hollow, and the chrome-ore, reducing agent, and flux are formed into round briquettes having a diameter a little less than the bore in the electrodes. These briquettes are fed into the furnace through the hollow electrodes and are thus subjected to the intense heat of the arc.

Manganese. Manganese likewise is reduced from its ores with silicon in an electric furnace.

Silicon. Silicon is reduced from silica rock with carbon in an electric-arc furnace. With petroleum coke and a careful selection of the silicon rock or sand, 96 to 97 per cent silicon can be made. A 3,000-kw. furnace operating at 120 volts will produce 5 to 6 tons of silicon in 24 hr.

CHAPTER XVII

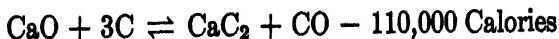
ELECTRIC FURNACES IN NON-METALLURGICAL INDUSTRIES

Electric furnaces are used in a number of cases because no other commercial means are available for producing the high temperatures required. A number of the furnace applications discussed in this chapter can be classed under this head.

CALCIUM CARBIDE

The manufacture of calcium carbide is one of the earliest electrochemical industries. Its industrial development goes back to about 1892 when Thomas L. Willson in America and Moissan in France independently developed commercial processes; indeed, they are said to have rediscovered its manufacture, for 30 years before, Wöhler, and still earlier Davy, had made calcium carbide on a small scale. The industry expanded with exceptional rapidity; in fact, in France the overproduction of calcium carbide led to a crisis in 1899, and many of the idle carbide furnaces were converted to the manufacture of ferrosilicon and other products.

Calcium carbide is made by the interaction of lime and carbon at the high temperature of the electric arc:



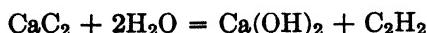
The action is reversible and according to the phase rule has one degree of freedom; that is, at a given temperature there is one definite pressure of carbon monoxide which corresponds to equilibrium. At 1,475° C. (2,677° F.) the equilibrium carbon monoxide pressure is 0.80 mm. mercury.¹ Above 1,500° C. (2,732° F.) calcium carbide decomposes into its elements but not so rapidly as it is formed or its manufacture would not be possible. Thompson² considers it improbable that

¹ M. de K. Thompson, *Proc. Am. Acad. Arts Sci.*, **45**, 431 (1910); *Met. Chem. Eng.*, **8**, 327 (1910).

² M. de K. Thompson, *Theoretical and Applied Electrochemistry*, p. 411. Macmillan Company, New York, 1925.

2,000° C. (3,632° F.) is exceeded in commercial practice, for high temperature would accelerate the decomposition of the carbide already formed.

Commercial calcium carbide is dark colored, but in the pure state it is colorless and transparent. When calcium carbide is treated with water, acetylene is formed:



The acetylene is used for illumination, for cutting and welding by oxyacetylene torches, and as a starting point for the synthesis of organic compounds such as acetic acid, acetone, and methanol. Calcium carbide is also used for the fixation of atmospheric nitrogen as cyanamide according to the equation



It is a strong reducing agent and is formed in the arcing zone of electric-arc steel furnaces when lime and a carbonaceous material are added to the charge. The fact that arc furnaces will form calcium carbide is claimed to be one of their points of superiority in steel refining. Calcium carbide is insoluble in all known solvents.

Raw Materials. The materials used in the manufacture of calcium carbide are carbon, in the form of coke, coal, or charcoal, and lime, to which may be added carbon from the electrodes.

As a source of carbon, anthracite coal has found wide application in England, but in the United States petroleum coke and to a much larger extent ordinary coke are used almost exclusively. Ash, phosphorus, sulphur, and moisture should be as low as possible. Coke with ash above 12 per cent is not desirable and that under 8 per cent is preferable. Charcoal as a source for carbon has the following advantages: it causes smoother furnace operation and enables a higher output to be reached than with coal or coke, and the carbide obtained is of the best quality in respect to gas yield and absence of impurities. However, charcoal is little used, for because of its low fixed carbon content (about 56 per cent) and its friability only about half the charcoal paid for enters into the furnace charge in a usable condition,³ which on account of its high price makes its use costly. Furthermore, the carbide produced from charcoal is not suitable for use in many modern acetylene generators.

³ C. Bingham and C. H. Bingham, "The Manufacture of Carbide of Calcium," *Welding Journal*, London, 1928.

If the carbide is to be used for acetylene production, phosphorus in the carbonaceous material is the most obnoxious impurity, for under the strongly reducing conditions in the furnace the phosphorus will appear in the carbide as a phosphide, which when treated with water in the generator forms poisonous phosphine, PH_3 . When acetylene is generated from a phosphorus-containing carbide it produces a haze of phosphoric acid around the burner when burned. Sulphur is not as objectionable as phosphorus, but if it exceeds a maximum limit it will cause difficulties with the acetylene burners.

The lime used is preferably a good quality of chemical lime made from a limestone containing at least 97 per cent calcium carbonate. As much as 1 per cent of magnesium oxide may be present with the production of a good grade of carbide, but it reduces the fluidity of the carbide and thereby may cause difficulty in tapping furnaces. It is preferable, therefore, that limestone with a magnesium oxide content of 0.5 per cent or less be used. Alumina also decreases the fluidity of the carbide but it is not so bothersome as magnesium oxide. Silica in the lime lowers the fusion temperature and thereby it increases production and facilitates the operation of tapping furnaces, but the percentage of calcium carbide in the furnace product is decreased. Limestone with silica content under 1.25 per cent for carbide manufacture is to be preferred.

Ingots Furnaces, Batch Type. In the early history of calcium carbide manufacture, the carbide was produced in ingot furnaces. It is now made in tapping furnaces, but a brief description of these earlier furnaces will be given.

In one type of ingot furnace a box of iron plate, lined with carbon, was mounted on wheels so that it could be moved easily in and out of the furnace housing. A carbon electrode was suspended in the housing above the box. Electrical connections were made to the carbon lining and to the electrode. The furnace had a funnel-shaped extension at the top lined with refractory. The charge was shoveled into this and heaped around the electrode. During a run it was necessary to raise the electrode from time to time as the carbide collected in the crucible. When the run was completed, the hearth conductor was disconnected and the furnace was wheeled away and allowed to cool. The charge was then removed and the carbide center was freed from large quantities of adhering carbon and lime.

The furnaces were of the smothered-arc type and were built in units of about 250 kw., requiring on an average about 55 volts. The ingots weighed nearly 900 lb. but contained only about 50 per cent good carbide. The yield, therefore, was low, a ton of 85 per cent commercial

carbide requiring a little over a ton each of carbon and of lime and over 100 lb. electrode carbon. The energy consumption was about 3 kw-hr. per lb. of 85 per cent carbide.

Horry Continuous Ingot Furnace. The Horry carbide furnace shown diagrammatically in Fig. 198 consisted of a slowly rotating drum-shaped furnace about 8 ft. in diameter and 3 ft. long. The ends of the drum consisted of two vertical discs held apart by a horizontal cylinder concentric with the axis of the furnace. Segments of cast-iron plates were bolted to the outer circumferences of the side discs, but only on the lower half, so that an annular space was formed. A vertical charg-

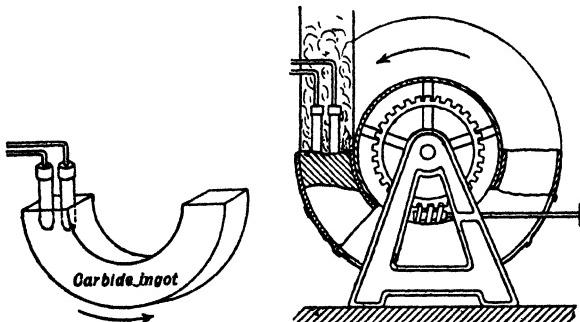


FIG. 198. Horry calcium carbide furnace.

ing shaft was placed tangentially over one end of this segment, and two electrodes were suspended in the lower part of this shaft. The charge was fed down the shaft around the electrodes. The current entered through one electrode and passed through a small portion of the charge and then out the other electrode. The electrodes were completely imbedded in the charge and were well protected from oxidizing influences. The furnace revolved slowly so that the carbide formed under the electrodes moved downward. A revolution was made in about 2 days. The carbide ingot formed, therefore, had the shape shown in Fig. 198. Opposite from the charging side the cast-iron plates were unbolted and removed and the carbide was removed. The plates were taken to the charging side and bolted in place for another half-revolution.

The feeding of the charge, regulation of the electrodes, and rotation of the furnace were taken care of automatically.

The furnace was of the smothered-arc type; it took a current of 4,000 amp. at 75 to 80 volts and had a daily production of 2 tons, which corresponded to an energy consumption of approximately 1.63 kw-hr. per lb. of carbide. The electrode consumption was about $4\frac{1}{2}$ to $6\frac{1}{2}$ lb. per ton of product.

Tapping Furnaces. Practically all the ingot carbide furnaces have been superseded by tapping furnaces. The furnaces themselves are usually of simple construction, but the automatic electrode regulators and charging devices and other accessory equipment may make a large unit quite complicated. The 12 carbide furnaces installed at Muscle Shoals were rectangular in shape, 12 ft. by 22 ft. by 6 ft. deep. They were large steel boxes lined with firebricks. Tapping furnaces are built in open- and in closed-top design; in the closed type the dust and gases can be collected and used. Recovered carbon monoxide is used for burning limestone to lime.

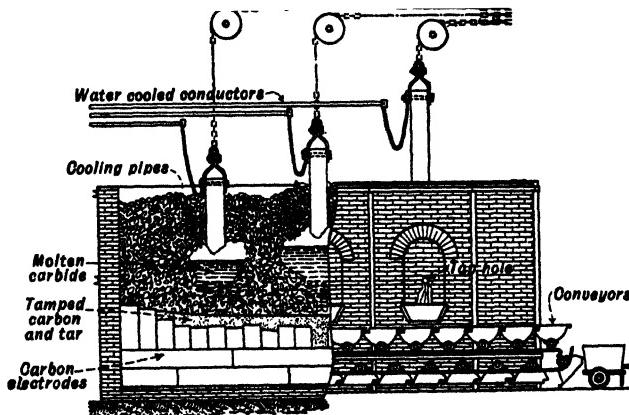


FIG. 199. A calcium carbide furnace.

In three-phase furnaces, the electrodes are suspended vertically in line or located at the points of a triangle. Electrical connection of the electrodes is three-phase delta or less commonly star connection with the hearth connected to the central point of the transformer. Heating is largely by resistance through the charge, but there is also some arcing between particles. Currents of 25,000 to 240,000 amp. per electrode or electrode bundle are being used. The operating voltage is from 110 to 125 volts.

Modern furnaces are charged in a continuous or intermittent manner by mechanical means. The molten carbide is tapped through one or more tap holes in the front of the furnace. American practice tends toward a single tap hole per furnace; European practice is to have a separate tap hole in front of each electrode, one of which is shown in Fig. 199. The molten carbide runs into cast-iron chills or bowl-like molds. When cool it is broken up, screened, and packed in air-tight containers unless it is to be consumed immediately at the plant. Figure 200 shows a modern carbide furnace.

The Miguet furnace has found considerable favor in Europe.⁴ The furnace proper is supported on pillars with the transformers located beneath the furnace. Forced air cools the transformers and the under part of the furnace. A single large electrode carries the current, which may be as high as 240,000 amp. The electrode is built up of prebaked carbon segments dovetailed and bolted together. The current is led to



FIG. 200. Calcium carbide furnace, located at Niagara Falls, Ontario; considered to be the world's largest electric furnace. (Courtesy American Cyanamid Company.)

the electrode by means of a number of separate circuits arranged around the furnace.

Energy and Materials Consumption and Distribution. Data on operation of carbide furnaces and their yields for European practice have been given by Taussig and others.⁵ For the production of 1,000 lb. of 85 per cent carbide there are required in the aggregate 980 lb. of lime, 650 lb. of coke, and 20 lb. of electrode. The average composition of commercial carbide from a large furnace was: calcium carbide 85.5,

⁴ P. Bunet, *Trans. Am. Inst. Elec. Engrs.*, **54**, 1320 (1935).

⁵ R. Taussig, *Die Industrie des Kalziumkarbides*, Wilhelm Knapp, Halle, Germany, 1930; F. Ullman, *Enzyklopädie der technischen Chemie*, II, Urban and Schwarzenberg, Berlin, 1928; E. Schlumberger, *Z. angew. Chem.*, **40**, 141 (1927); H. Danneel, *Z. Elektrochem.*, **36**, 474 (1930).

calcium oxide 8.2, carbon 2.1, magnesium oxide 0.5, silica 3.2, sulphur 0.3, and alumina plus iron oxide 0.2 per cent.

Furnaces are built in sizes up to 25,000 kw-a. and over, producing about 17.5 to 20 lb. calcium carbide per kw-day.

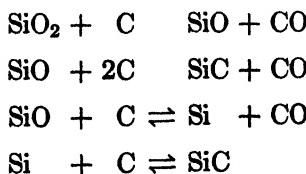
SILICON CARBIDE

Silicon carbide, SiC, is better known by its trade names "Carborundum," "Crystolon," and "Carbolon." It is produced along with other compounds when silica is reduced by carbon at high temperatures. The reaction as regards raw materials and end products may be represented by the equation:



Silicon carbide was discovered accidentally in 1891 by Acheson when he attempted to form diamonds by dissolving carbon in molten clay. Instead of diamonds he obtained blue crystals of silicon carbide, which he believed to be made up of carbon and corundum (alumina), and he therefore named the new product Carborundum. Its value as an abrasive was soon evident, and later it was found to be a valuable refractory material also.

Silicon carbide is made commercially in large quantities by heating a suitable mixture of carbon and silica in a resistance furnace. At the temperature of the furnace a number of reversible reactions may take place as shown by the following equations, although not all the reactions have been definitely established.



Raw Materials. The chief raw materials for silicon carbide manufacture are silica and carbon. Little difficulty seems to be experienced in obtaining a good grade of silica sand containing above 98 per cent SiO_2 . The carbon is supplied by a good grade of anthracite coal, coke, or petroleum coke. The anthracite and coke should be low in sulphur and ash. Sulphur produces unpleasant sulphur dioxide fumes during operation, and iron oxides and alumina are likely to interfere seriously with the uniformity of ceramically bonded products made from the grain. The sand and carbon are mixed in the proportion corresponding roughly to the molecular ratios given in the first equation.

Sawdust is generally mixed with the charge; it increases the porosity of the charge at furnace temperatures, making it easier for the carbon monoxide and other volatile products to escape. Salt is used to convert the metallic oxides, especially iron, to volatile chlorides. A typical charge based on figures given by Tone⁶ consists of sand 54.4, coke 35.1, sawdust 7, and salt 3.5 per cent.



FIG. 201. A silicon carbide furnace. (*Courtesy The Carborundum Company.*)

Furnaces. The general arrangement of a silicon carbide furnace is shown in Fig. 169b, page 389, and an installation in Fig. 201. At the Carborundum Company,⁷ the furnace consists of a U-shaped trough of firebrick, 6 ft. across, 6 ft. deep, and 40 ft. long. The brick trough is supported on piers in such a way that the furnace bottom is air cooled. At each end of the trough is a reinforced brick pier through which the water-cooled graphite electrodes pass. In charging the furnace the raw materials are loaded into the trough until the level of the electrodes is reached. A core of granular graphite serving as the current carrier or resistor is then run through from one electrode to another. The remainder of the charge is heaped over the graphite core, and when completed consists of about 70,000 lb. of material in the form of a cylinder.

⁶ F. J. Tone, *Trans. Am. Electrochem. Soc.*, 7, 243 (1905).

⁷ Anon., *Chem. & Met. Eng.*, 31, 501 (1924).

There is no noticeable change after the current is turned on, except that the charge gradually sinks in volume, and flames of carbon monoxide appear flickering over the surface of the charge and between the loosely set firebrick of the walls and bottom.

The mass after completion of a run is composed of several concentric cylinders or strata. On top is a loose crust of siliceous material and unconverted charge. This is returned to the mixing room, or if badly caked with volatile impurities from the hot zone it is discarded. Next comes a layer of partly converted mix and poorly crystallized silicon carbide. This is known as "fressand" and is utilized in refractory cements for lining brass and other furnaces. Inside of this and gradually merging into it is the high-grade silicon carbide of abrasive and refractory quality. After being allowed to cool the mass of intercrystallized silicon carbide is broken up with bars into smaller pieces which are transported to the crushers.

Pure silicon carbide is colorless, but the furnace product is green, blue, or black, and iridescent. The iridescence, seen by reflected light, is due to a thin film of silica which can be removed by treatment with hydrofluoric acid. The green or blue color is seen by reflected light.

A 1,500- to 2,000-kw. furnace producing 10,000 to 16,000 lb. in a run of 36 hr. requires an initial voltage of 250 to 300 volts. As the conducting core heats up, its resistance drops and the voltage must be reduced to prevent the current from becoming excessive. At the end of a run the voltage is about 200 volts. The current at the start of a run is about 6,000 amp. and increases gradually to 20,000 amp. The average power required is about 3.5 kw-hr. per lb. of silicon carbide. The theoretical yield is estimated to be 1.76 kw-hr. per lb.

The temperature of silicon carbide formation (at which the vapor pressure of carbon monoxide is 1 atmosphere) is about 1,650° C. (3,000° F.); its dissociation temperature (at which the vapor pressure of silicon equals 1 atmosphere) is above 2,500° C.⁸ (4,532° F.). The ideal operating condition would be such that all parts of the charge are heated to a temperature between these two limits.

A study of the temperatures of a commercial silicon carbide furnace has been made by Ridgway,⁹ who came to the conclusion that for the furnace investigated the operating temperature for the development of the silicon carbide zone was between the limits of 1,950 and 2,050° C. (3,542 and 3,722° F.), adding, however, that this does not preclude the possibility of producing the same result by higher temperatures in shorter time, or with lower temperatures with longer time. Ridgway

⁸ F. J. Tone, *Ind. Eng. Chem.*, **23**, 1315 (1931).

⁹ R. R. Ridgway, *Trans. Electrochem. Soc.*, **61**, 225 (1932).

also comes to the conclusion that during this stage of the run the electrical power flows through the silicon carbide ingot as well as through the carbon core. He found the maximum temperature of the central core to be 2,550 to 2,600° C. (4,622 to 4,712° F.); that of the middle of the ingot wall 2,080° C. (3,776° F.); and that of the border firesand zone, 1,950° C. (3,542° F.). Figure 202 shows the temperatures of the silicon carbide zone as reported by Ridgway.

The formation of silicon carbide from the raw materials is an endothermic reaction. The building up of a large crystalline ingot of carbide

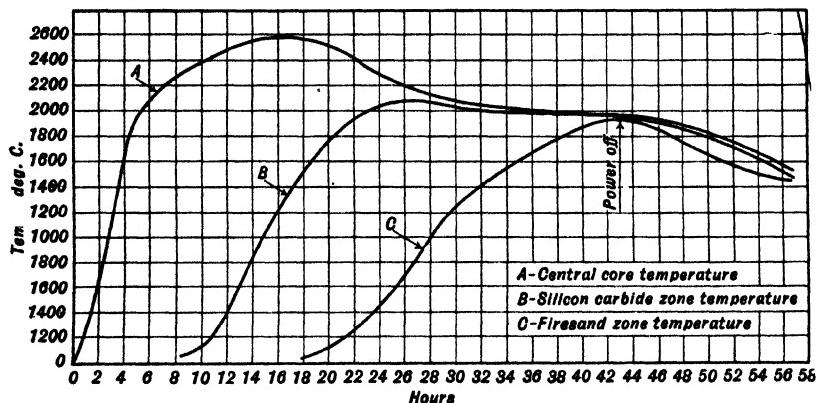


FIG. 202. Silicon carbide zone temperatures vs. hours of operation.

in a resistance furnace is a time-temperature function. The formation of large crystals can be brought about at high temperatures in a relatively short time or at lower temperatures in a longer time. The formation of a large crystalline ingot of silicon carbide involves the vaporization of crystals in the inner temperature zone and the recrystallization of the mass by growth of the large crystals at the expense of the small ones. The vapor of silicon carbide or its dissociation products supplies material for the growth of larger crystals.

Firesand includes considerable amounts of amorphous or poorly crystallized material and is formed as a by-product in the furnace zone outside the crystalline silicon carbide. It is not as refractory as the crystalline carbide and oxidizes more easily. It is suitable for use for furnace bottoms and for crucibles where the furnace atmosphere is of a reducing nature.

Processing of the Silicon Carbide. The carbide is ground in dry pans about 7 ft. in diameter. The two mullers weigh about a ton each and are equipped with chilled iron or manganese steel tires to resist abrasion, but the wear on the grinding equipment is very severe.

The crushed material is put through an acid (H_2SO_4) wash in lead-lined tanks and may be treated further with a hot caustic solution. The chemical treatment removes silicon, iron, silicides of iron, aluminum, and graphite.

Iron is reintroduced by abrasion of containers and in subsequent grinding operations and is removed by means of a magnetic pulley or a high-intensity magnetic separator.

Some of the silicon carbide is merchandised as dry powder or grains, but the greater part is manufactured into grinding wheels, abrasive stones, coated cloth and paper, refractories, and electrical resistors.

For grinding wheels several different bonding agents are introduced, depending upon the purpose for which the wheels are to be used. A vitrified binder of the general nature of porcelain is a common agent. The abrasive grain, clay, and other bond, if needed, are mixed with water. In the wet or puddling process the mixture is stirred for several hours in a hemispherical tub for the purpose of securing a thorough mixture and of removing any entrapped air. The mixture is then poured into metal ring molds supported on plaster "batts" and lined with heavy paper. The batts remove most of the water by absorption before the wheels are put in the drying oven. In the dry-press process the ingredients with much less water are introduced in tumbling barrels and turned until the abrasive grains are coated with bonding material. The mixture has the general consistency of molding sand. The mixture is transferred to steel molds and subjected to hydraulic pressure. When dry, the wheels made by either process are fired in a kiln to become vitrified. In another method, sodium silicate (water glass) is mixed with the sized silicon carbide grain. The "green" shaped wheel is dried and then baked at about $260^\circ C.$ ($500^\circ F.$), which hardens it into a firm unit. For thin wheels rubber is mixed with the grains, and the mass is rolled into sheets of the desired thickness. The wheels are stamped from this and are then vulcanized. Shellac and synthetic resins such as Redmanol are similarly used for making thin cutting wheels.

Grains of silicon carbide are also fixed with glue to the surfaces of paper and cloth used for grinding and polishing purposes.

For refractory manufacture the silicon carbide grains are carefully screened and different sizes are mixed in proportions calculated to give a dense product. The silicon carbide is mixed with about 8 per cent plastic refractory clay as a bonding agent, and the refractory shapes are formed from the damp mass. The dried shapes are fired in kilns to cone 14 (approximately $1,390^\circ C.$ or $2,534^\circ F.$).

Recrystallized Silicon Carbide. For exceptionally severe duty, refractories are prepared by the Carborundum Company without any

clay or other permanent bond. A temporary bond of tar or pitch holds the bricks in shape until they have developed sufficient strength by recrystallization. The "green" bricks are placed in the regular silicon carbide furnace in the mix surrounding the granular graphite core. As the temperature rises, the tarry bond distils off; and at the higher temperatures some of the silicon carbide grains volatilize and recondense or recrystallize in an interlocking manner, giving the brick exceptional strength when put in service at high temperatures. Recrystallized silicon carbide bricks are sold under the trade name of "Refrax."

Silicon carbide refractories are exceptionally refractory and possess the valuable property of maintaining high mechanical strength at furnace temperatures. Tests have shown that at 1,300° C. (2,372° F.) the cross-breaking strength is practically the same as at atmospheric temperatures.¹⁰ The heat conductivity of the refractories is also high.

Silicon carbide is also used for the manufacture of electrical heating resistors, such as "Globar," but manufacturing details have not been disclosed.

BORON CARBIDE

A method for the commercial production of boron carbide has been described by Ridgway.¹¹ On the basis of chemical analysis and X-ray studies, Ridgway concludes that the formula for boron carbide is B₄C.

The raw materials are boric acid and a high-purity coke. The boric acid is first dehydrated by heating it to fusion, which is carried on outside the final furnacing operation. The anhydrous glass and the coke are then placed in a special resistance furnace, in much the same way that sand and coke are heated in a silicon carbide furnace. A central heating core is provided, and the surrounding mixture is heated to 2,500 to 2,600° C. (4,532 to 4,712° F.). A cylindrical ingot of boron-impregnated crust encloses a zone which consists largely of freely developed crystals of boron carbide. Inside this zone is a zone of molten carbide which fuses and forms a thick ingot. The separated product is sorted and classified for various uses. A typical furnace product contains 97 per cent boron carbide, 2 per cent boron, and small amounts of other materials.

Boron carbide is exceptionally hard, having a hardness greater than silicon carbide but less than diamond. This hardness has led to the substitution of boron carbide lapping powder for diamond dust in various commercial operations. Boron carbide is inert to all solutions of

¹⁰ M. L. Hartmann and W. A. Koehler, *Trans. Am. Electrochem. Soc.*, **40**, 457 (1921).

¹¹ R. R. Ridgway, *ibid.*, **68**, 117 (1934).

acids and alkalies in all concentrations. The oxidizing acid mixtures are without effect. The density of boron carbide is approximately 2.52.

Boron carbide is comparatively new as a commercial item, and it is probable that a number of new applications will be found. The industrial applications of boron carbide depend upon its hardness, its ability to be melted to a liquid phase and then cast to desired shape, and its freedom from pores. It is used as an abrasive and polishing powder. In cast form it is especially suited for use as pressure blast nozzles. There is also promise of application of the molded product to jewel-type bearings.

FUSED ALUMINA

Fused alumina is made by fusing bauxite in an electric furnace. It is put on the market under such trade names as "Alundum," "Aloxite," and "Exolon." Like silicon carbide, it finds extended use as an abrasive and as a refractory.

One process of manufacture, that employed by the Carborundum Company, has been described by Tone.¹² The bauxite raw material is calcined to remove about 30 per cent of moisture and is then mixed with ground coke and iron borings. The furnace consists of an unlined water-cooled steel shell about $7\frac{1}{2}$ ft. in diameter and 6 ft. high, the bottom lined with carbon. The top of the furnace is open, the electrodes are suspended vertically in the furnace from the top. The mixture is fed in, and as it fuses, the electrodes are raised and more charge is added, thus gradually building up an ingot. The fusion is accomplished with a muffled arc. When the furnace is filled, the electrodes are raised, the power is shut off, and the ingot is allowed to cool. The furnaces are mounted on trucks which travel on rails so that the furnace with its ingot can be transported to other parts of the plant where the ingot is removed from the furnace. One type is shown in Fig. 203.

A furnace operates at about 100 volts and takes about 2,500 amp. The furnace temperature is 2,000 to 2,200° C. (3,632 to 3,992° F.).

At the high furnace temperature practically all oxides in the charge are reduced by the carbon, with the exception of the alumina and some titanium oxide, although the last will reduce quite readily unless considerable care is taken. The reduced metals consisting mainly of iron and silicon, but also some titanium, phosphorus, sulphur, and aluminum form an alloy and settle for the main part to the bottom of the furnace as a button, though some of the alloy remains dispersed throughout the ingot, owing to the turbulence in the melt and the fine state of subdivision

¹² H. E. Howe, Ed. *Chemistry in Industry*, I, pp. 21-33, The Chemical Foundation, Inc., New York, 1924.

of the particles which it is desired to settle out. The separated alloy is useful as a low-grade ferrosilicon.

One method for breaking up the ingot of fused alumina to smaller lumps is to use a "skull cracker," consisting of a heavy manganese steel ball which is raised with a crane and electromagnet or cable and winch until it is some distance above the ingot and is then allowed to



FIG. 203. Furnace for melting bauxite. (*Copyrighted, National Geographic Society. Reproduced from the "National Geographic Magazine" by special permission.*)

drop. Several such blows break the ingot to sledge-hammer size, after which it can be handled by jaw crushers and rolls.

The ground alumina is subjected to magnetic separation to remove the ferrosilicon which did not settle out. The iron added in the charge serves to increase the iron content of this ferrosilicon to a point to make it sufficiently magnetic for this purpose. The fused alumina analyzes about 96 per cent Al_2O_3 . Some of the impurities remaining in the alumina increase its toughness.

The grain is washed and sometimes is treated chemically and screened to various sizes. Like silicon carbide, the fused alumina is made into grinding wheels and stones with various bonding agents, and is used for making refractory shapes. As a refractory it has found special applica-

tion in muffles on account of its fair heat conductivity and especially in wire-wound muffles where the high electrical resistance of fused alumina prevents electrical short circuiting of the element.

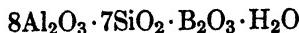
Alumina is also made into molten-cast alumina refractories sold under the trade name "Monofrax." The manufacturing process is similar to that for producing fused mullite refractories described below. A modified product called "Monofrax H," consisting of beta-alumina, is used for lining electrolytic cells for producing magnesium.

FUSED MULLITE

Mullite is a highly refractory material of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. No deposits capable of being commercialized have been found, but the material does occur in nature. It is formed when an alumino silicate is heated above $1,545^\circ\text{ C}$. ($2,813^\circ\text{ F}$.). It is a constituent of porcelains and many other clay wares that have been subjected to a high temperature. It can also be prepared by heating any one of a group of alumino silicates, each of the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, but differing in their crystalline structures, called andalusite, cyanite, and sillimanite, respectively. The conversion is represented by the reaction



It is also prepared commercially by heating dumortierite,



Before the work by Bowen and Greig was available, there was considerable misunderstanding about the relation these minerals bore to one another, and as a result the name "artificial sillimanite" or simply sillimanite was used to designate that material now known as mullite.¹³

Mullite is made by the Corhart Refractories Company by fusing together several alumino silicates in an electric furnace. The raw materials used are diaspores from Missouri and Kentucky, containing from 9 to 18 per cent SiO_2 and kaolin (clay). Diaspore when pure has essentially the composition $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; kaolin, that of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The kaolin is used to adjust the Al_2O_3 - SiO_2 ratio to approximately that in mullite. The clay is ground and calcined in a gas-fired rotary kiln and is then sent to one of a number of uniformizer bins.

The manufacturing process for making cast blocks has been described by Schroeder.¹⁴ The clay and diaspore mixed in the proper proportion

¹³ The relations these various minerals bear to one another and their physical properties are discussed by the author in *Chem. & Met. Eng.*, 35, 86 (1928).

¹⁴ F. W. Schroeder, *Ind. Eng. Chem.*, 23, 124 (1931).

on the basis of chemical analyses are fed to the furnace at a rate of about 750 lb. per hr. for the smaller furnace. The electric furnaces used for the manufacture of these refractories are of the dipping-electrode resistance type. The first furnace installed was a 500-kv-a. unit with a capacity of 600 lb. refractory per hour. Another furnace built later uses 750 kv-a. The electrodes are 8-in. graphite, and the load is balanced manually among the three phases.

The furnace forms its own refractory lining by the natural cooling of the melt adjacent to the steel walls. The liquid between the electrodes is probably in the neighborhood of 2,200° C. (4,000° F.), for the stream of tapped liquid gives a reading of approximately 1,870° C. (3,400° F.).

At 2-hr. intervals the furnace is tapped and the melted refractory is poured into molds. For the molds, high-silica sand is mixed with linseed oil and slabs are formed which are baked in ovens. They are then trimmed to size and are built into molds of the desired shape and size, using an organic binder. The molds are allowed to dry and as required are set up in cans with an insulating material packed around them. The molds disintegrate during the casting process.

After casting, the cans are allowed to stand for a while, the fonts are knocked off, and the cans are carried to storage where the cast blocks anneal for 6 to 10 days. After the annealing period the castings are dumped, cleaned, and sent to the shipping room or storage, while the mixture of sand and insulating powder in the cans is reclaimed in an air separator system.

The refractory obtained from the electric furnace casting process has a pyrometric cone equivalent of cone 37 (a softening point of approximately 1,820° C., or 3,300° F.). It has a vitreous, non-porous body and a linear coefficient of expansion approximately one-half that of first-class firebrick. The finished blocks cannot be chipped, cut, worked, or shaped; It is possible to grind them on Alundum or Aloxite wheels, but the process is extremely slow.

Fused mullite refractories find chief application for use in glass tanks but can be used in a number of other cases where temperature conditions are very severe, though they spall fairly readily when subjected to thermal shock.

GRAPHITE

Carbon exists in three forms, diamond and graphite, the crystalline varieties, and amorphous carbon. Graphite is stable at all temperatures. The diamond is theoretically unstable at all temperatures; however,

unpublished reports indicate that in the absence of oxygen the diamond is "stable" at temperatures up to red heat. The amorphous variety carbon is unstable at all temperatures.

Natural graphite was known in early times and is used at present in large quantities in the manufacture of graphite crucibles. Artificial graphite was discovered and its manufacture developed by Acheson, and the term "Acheson graphite" is used by some as synonymous with artificial graphite.

According to the theory of graphite formation, carbides are first formed by the interaction of amorphous carbon with metallic and siliceous oxides present as impurities or introduced specially for that purpose. At higher temperatures the carbides are decomposed, and the metals or metalloids are distilled off, leaving graphite behind. Coke, used as the raw material for graphite production, contains sufficient ash to produce full conversion to graphite. The action is a catalytic one, and the actual amount of ash or other catalyzing agent above a certain minimum amount is immaterial for complete conversion. The furnace process can be so conducted that conversion is complete, with no amorphous carbon admixed with the graphite. The volatilization subsequent to the graphitization is a purifying process, and it is possible to use a relatively impure raw material and yet obtain a very pure graphite.

Artificial graphite¹⁵ is prepared in electric resistance furnaces in which the charge forms the resistor. The furnace is somewhat similar in construction to that of a silicon carbide furnace, rectangular in shape, the electrodes being introduced through the ends. The side walls are built up of refractory bricks laid without bond or of concrete blocks. Bus-bars come up through the floor and make direct contact with the electrodes. Single-phase alternating current is used with an initial voltage of 200 volts, dropping off to 40 volts at the end of the run. The furnaces are built in 1,500-kw. sizes; they take close to 4,000 amp. at the start and 9,000 amp. toward the end of the run. A run requires 24 to 48 hr. The core or load is 30 ft. long by 6½ ft. square, and weighs up to 50,000 lb. The furnace temperature in the charge is 2,200° C. (3,992° F.) or higher.

Furnace operation differs according to whether preformed objects such as plates or electrodes are to be graphitized or whether graphite is to be prepared in bulk in loose form. Preshaped objects are packed in the furnace between the end electrodes as closely as possible and the space between is filled with packing, a finely ground carbonaceous material. Figure 204 shows a method of packing electrodes in the furnace.

¹⁵ E. C. Sprague, *Trans. Electrochem. Soc.*, 70, 57 (1937).

A similar type of furnace is used for graphitizing powder. The raw material may be petroleum coke, anthracite coal, or even coal waste. The finely crushed material is loaded into the furnace, and on passage of the current innumerable small arcs are formed between the particles.

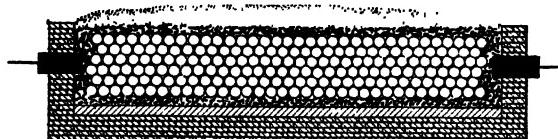


FIG. 204. Section of graphite furnace for round electrodes.

Heating is continued until all impurities have been volatilized; the time required therefore depends upon the purity of the raw material.

FUSED QUARTZ

Fused quartz is made in two forms, transparent and opaque. The opaque variety has been available for many years for laboratory ware, sulphuric acid evaporators, and other equipment where glass has not proved sufficiently refractory. Clear fused quartz is used for lenses and electric-light bulbs for special purposes where transmission of ultra-violet light is desirable. It is also used for special laboratory ware. Both varieties of fused quartz are characterized by their refractoriness and extremely low coefficient of thermal expansion.

For manufacture of the opaque variety, a rod or plate of carbon is imbedded in pure silica sand containing 99.5 per cent or more of SiO_2 . The carbon is heated by an electric current, resulting in the formation of a crude tube of fused quartz. Pure quartz has a melting point of $1,756^\circ \text{C}$. (approximately $3,200^\circ \text{F}$.), but it must be heated to $2,000^\circ \text{C}$. ($3,632^\circ \text{F}$.) to make it fluid enough to work. Silicon carbide is formed next to the carbon rod, but this adheres to the carbon. The tubes are worked up into various types of laboratory ware by modified glass-working methods. The relatively crudely fashioned articles are trimmed and polished by the aid of abrasives and a hot flame such as the oxyhydrogen flame.

The manufacture of clear fused quartz has been described by Berry¹⁶ and by Devers.¹⁷ Raw material of the very highest quality is required, so that water-clear crystals of quartz are selected, containing probably

¹⁶ E. R. Berry, *Chem. & Met. Eng.*, **30**, 715 (1924); and *Trans. Am. Electrochem. Soc.*, **45**, 511 (1924).

¹⁷ P. K. Devers, *Ceram. Age*, **15**, 324 (1930).

less than 0.2 per cent impurity. If the crystals are incrusted with iron oxide or other impurities, as at least part of any quartz crystal usually is, they are given an acid wash. The crystals are broken, and the best parts are selected for the fusion. The clean quartz crystals are packed as densely as possible in a graphite or carbon crucible so that during the



FIG. 205. Inserting trays of quartz crystals into a vacuum furnace for making clear fused quartz. (Courtesy General Electric Company.)

cracking of the crystals, which is bound to occur as the temperature is raised, the parts cannot separate to allow small amounts of gas to enter the many crevices and thus form bubbles in the melt.

The tightly packed crucible is placed in a modified vacuum furnace of the electrical resistance type and the temperature is raised as quickly as possible above the melting point of the crystals, which is about 1,800° C. (3,272° F.). During this fusion, which requires not over 45 minutes, the pressure in the furnace is kept as low as possible. The energy consumption is 3 to 8 kw-hr. per lb. of quartz. Figure 205 is a top view of a melting furnace.

The product from the first fusion is a clear transparent slug of silica as shown in Fig. 206, containing a few bubbles varying in size from a pin point to 2 or 3 mm. in diameter. This slug is placed in another graphite crucible suspended in a vertical carbon tube furnace. A graphite piston that just fits the inside of the crucible is placed on top, and a plunger is attached to the piston. The slug is again brought to a fusion and the



FIG. 206. A disc of fused quartz in the rough as taken from the furnace. (*Courtesy General Electric Company.*)

bubbles are largely collapsed by the weight. The quartz is then extruded in various forms such as rods, tubes, and ribbon.

Another method developed more recently for making tubing, rod, ribbon, or similar shapes is to form a heavy-walled hollow slug in an open-air carbon tube furnace, and, when the mass is soft, to push a graphite spike through the center of the mass. The heavy-walled hollow slug is then anchored to the revolving base of one end of a pulling machine and to a swivel joint traveling on a rack and pinion at the other end. Six to ten oxyhydrogen burners are then played on the top of the slug, which is drawn out slowly into long lengths of the desired dimensions.

When it is desirable to obtain large masses free from bubbles, the quartz is fused in a specially designed vacuum furnace that will also withstand high pressures. The furnace is constructed of very heavy cast-steel walls and has a cover 4 in. thick. The vacuum fusion is carried out as before, and when it is complete the vacuum valves are closed and nitrogen gas at a pressure up to 1,100 lb. per sq. in. is forced into the furnace as rapidly as possible in order to avoid chilling before the bubbles in the fused mass have been reduced to their minimum size.

PHOSPHORUS AND PHOSPHORIC ACID

Phosphorus. Phosphorus is produced by the electrothermal reduction of bone ash, phosphate rock, or crude phosphoric acid with a siliceous slag and a carbonaceous reducing agent. The reaction may be represented by



One form of furnace, shown diagrammatically in Fig. 207, consists of a gas-tight iron cylinder lined with a refractory material. Two carbon electrodes enter the furnace near the bottom, and arcs pass between the electrodes. In a modification of this furnace the electrodes enter the upper part of the furnace and the charge receives its heat by radiation. The phosphorus distils off and is collected under water in copper containers. Distillation begins at $1,150^\circ \text{C}$. ($2,100^\circ \text{F}$.) but requires $1,500^\circ \text{C}$. ($2,730^\circ \text{F}$.) for its completion.

Phosphoric Acid. Phosphoric acid, H_3PO_4 , is likewise made by electrothermic reduction of phosphate rock with silica and coke. Elemental phosphorus is first formed as indicated in equation 1 above, but, instead of being conducted away as a vapor out of contact with air, the vapor and the carbon monoxide formed are burned in the upper part of the furnace with oxygen from air, admitted under carefully controlled conditions, to form phosphorus pentoxide, P_2O_5 , and carbon dioxide. The furnace temperature is about $1,600^\circ \text{C}$. ($2,912^\circ \text{F}$.) The gases are conducted away from the furnace and cooled to the proper temperature, and the phosphorus pentoxide is hydrated to phosphoric acid by means of an atomizing water spray. Part of the concentrated phosphoric acid is

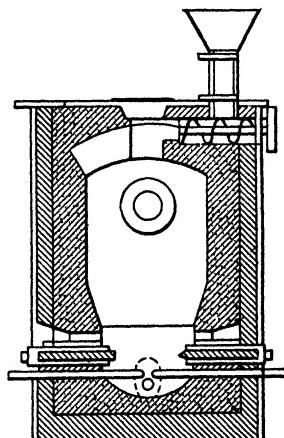


FIG. 207. Phosphorus furnace.

collected in hydrating and cooling towers, but the greater part is recovered by means of Cottrell precipitators. The energy consumption is in the neighborhood of 2.3 kw-hr. per lb. of phosphorus pentoxide. A sectional view of a furnace is shown in Fig. 208. Details of furnace de-

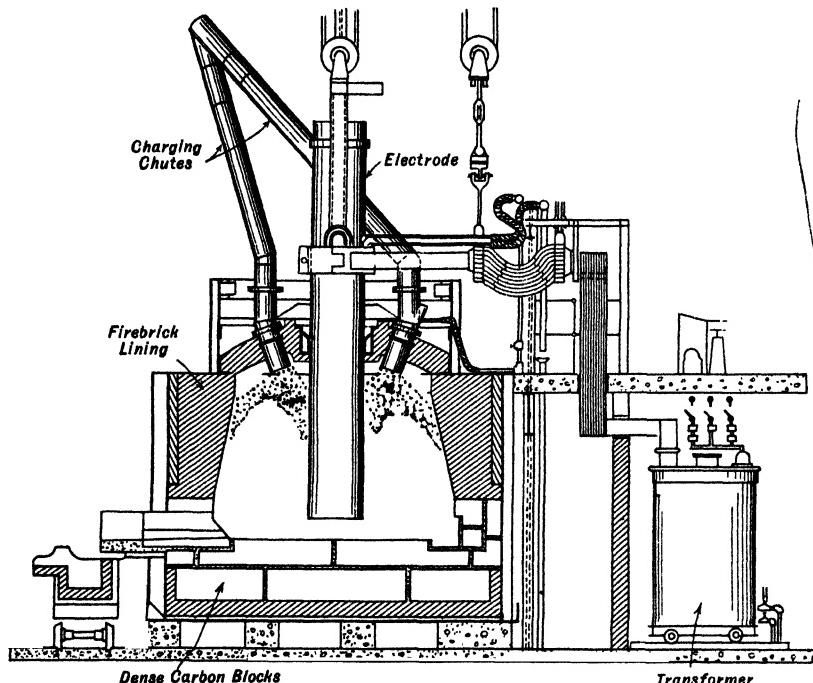


FIG. 208. Electric phosphate smelting furnace. (*Courtesy Chemical and Metallurgical Engineering.*)

sign have been described by Curtis and Heaton¹⁸ and operating details by Curtis.¹⁹

CARBON BISULPHIDE

Considerable amounts of carbon bisulphide, CS_2 , are made electro-thermally although the major portion is made in clay or iron retorts externally heated. The electrolytic process is used at Penn Yan, New York. The furnace as originally constructed was described by Taylor.²⁰ The furnace as now constructed is shown diagrammatically in Fig. 209. It is of the resistance type, circular in horizontal section, 8 ft. in diameter

¹⁸ H. A. Curtis and R. C. Heaton, *Chem. & Met. Eng.*, **45**, 536 (1938).

¹⁹ H. A. Curtis, *Chem. & Met. Eng.*, **42**, 320 (1935).

²⁰ E. R. Taylor, *Trans. Am. Electrochem. Soc.*, **1**, 115 (1902); **2**, 185 (1902).

at the bottom. The electrodes, 4 in number, placed 90° apart, are at the base of the furnace. They are covered with resistor carbon which incidentally protects the electrodes against wear. Charcoal is fed in at the top and recovers heat from the rising carbon bisulphide vapors that otherwise would be lost. Molten sulphur is introduced into the furnace below the electrodes.

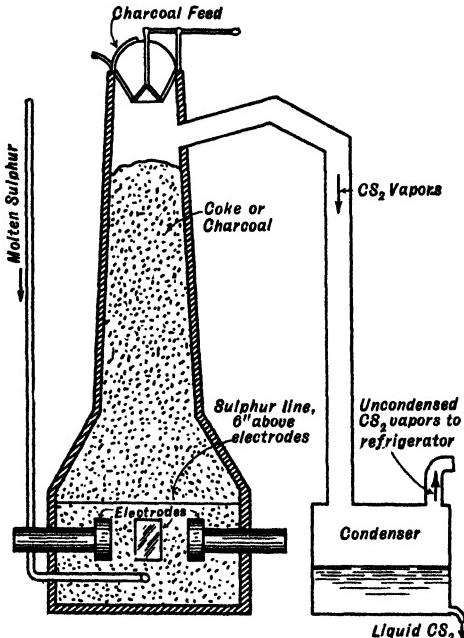


FIG. 209. Carbon bisulphide furnace.

At the furnace temperature the charcoal reacts with the sulphur to form carbon bisulphide, which passes out through a pipe near the top and is collected in a condenser.

The furnace is fed with two-phase current and consumes 250 kw. at 48 volts under normal load.

ELECTRIC HEAT-TREATING FURNACES

In recent years resistance-type electric furnaces have found considerable application even where high temperatures are not required. In practically all these applications the electric furnaces are in direct competition with fuel-fired furnaces. Electric furnaces are used for heat treating of metals, firing ceramic wares, and glass annealing. Their main advantages are their ability to turn out a better-quality product or

to reduce rejects and seconds, as a result of uniform temperature, close temperature control, and freedom from soot or cinder particles. In addition, they offer the advantage of pleasant working conditions. All these advantages must, however, be balanced against a higher fuel cost per pound of ware except perhaps in a few isolated instances, but the over-all operating cost of electric furnaces may be lower than in fuel-fired furnaces.

For resistors, metal ribbon and "Globar" resistors are widely used. The metal resistors are commonly of the nickel-chromium alloy type.

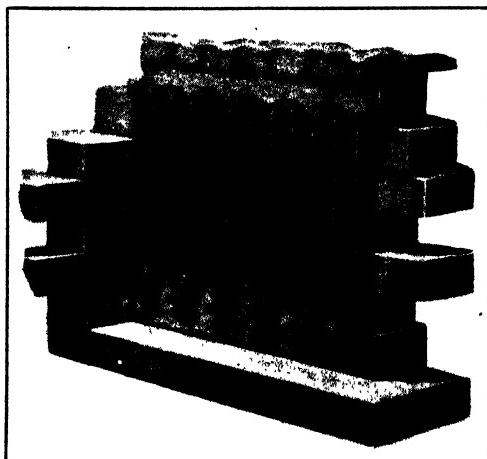


FIG. 210. Metal resistor as used in a pottery kiln. (*Courtesy Electric Furnace Company.*)

"Globar" is a trade name for a special brand of silicon carbide shaped into suitable resistors. Metal resistors are commonly in the form of ribbon, on account of the greater radiating surface exposed. Cast resistors, specially designed to give a large radiating surface, are also used. Figure 210 shows cast resistors as used for whiteware kilns. Other materials used as resistors are listed in Table XXX.

TABLE XXX

MAXIMUM WORKING TEMPERATURES OF VARIOUS TYPES OF FURNACE RESISTORS

	°C.	°F.		°C.	°F.
Tungsten	1,870	3,400	Kanthaloy	1,350	2,460
Molybdenum	1,870	3,400	Fe-Cr-Al	1,316	2,400
Carbon	1,870	3,400	Nickel chromium	1,100	2,000
Silundum	1,870	3,400	Aluminum steel	870	1,600
Platinum	1,650	3,000	Nickel	760	1,400
Globar	1,510	2,750	Iron	320	600

Resistance Furnaces. Electric resistance furnaces have found considerable application for annealing of various types of metals. For all commercial applications resistors of nickel-chromium alloy have a sufficiently high temperature range. The term "annealing" as applied to the ferrous alloys implies relatively slow cooling. Usually the annealing requires a rate of cooling slower than that obtained in air. In many cases the annealing follows some operation conducted at room tempera-



FIG. 211. Electric annealing furnace, car tunnel type. Rated at 240 kw., 220 volts, three-phase. Furnace is 12 ft. long. (Courtesy General Electric Company.)

ture, or the work is permitted to cool, for the sake of convenience, before it is annealed. Consequently the annealing furnaces may be required to heat the ware to a certain temperature and then to allow it to cool slowly. The period of the cycle is measured in hours and sometimes in days.

Figure 211²¹ shows an installation of a car-bottom resistor furnace, rated at 240 kw., 220 volts, three-phase. The charge is placed on the car bottom, and the unit is then pulled into the furnace. The hearth is 12 ft. long and 4 ft. 6 in. wide, and a full charge of castings weighs about 10 tons. The charge is heated to 900° C. (1,652° F.). The length of the heating cycle is 12 hr. The charge is then cooled to 700° C. (1,292° F.)

²¹ Taken with permission from N. R. Stansel, *Industrial Electric Heating*, John Wiley & Sons, New York, 1933.

during the following 12 hr. The capacity of the furnace is 10 tons of castings per 24 hr. The average operating efficiency is 270 kw-hr. per ton (2,240 lb.).

No attendance is required during the heating or cooling period. The temperature is under the control of an automatic temperature regulator, and a time clock serves to disconnect the power at the proper time. It is generally the practice to schedule the operation of the furnace so that it comes at the off-peak period of the 24-hr. load chart.

In order to distribute the heat in the oven uniformly, forced air circulation may be used. Cooling pipes through which cool air is forced may also be placed in the oven.

Annealing resistance furnaces are constructed in the batch and the continuous types, some of which are designed for temperatures up to 2,000° C. (3,630° F.).²²

Salt Bath Furnaces. The salt bath furnace of the resistance type is finding wide use in the heat treatment of metals. One type of furnace is shown in Fig. 212. A pair of electrodes is immersed in the salt, which is a conductor in the melted state. The electrodes are closely spaced, and an alternating current of 5 to 25 volts is impressed across them. The current flowing between the electrodes heats the salt in its path. The electrodes are placed along one side of the bath, to provide a free working space. The location and design of the electrodes are such as to create electromagnetic forces which automatically circulate the salt bath, and thus a uniform temperature is maintained throughout. A thermocouple immersed in the bath automatically controls the temperature. Suitable salt mixtures are available for various kinds of heat treatment, such as annealing, case hardening, tempering, and quenching.

Two methods are used for starting the furnace. In one, carbon rods are placed between the electrodes in the empty furnace and then covered with salt. The current heats the electrodes to incandescence, and the salt is melted. In the other, a pool of molten salt is made in the furnace with an oxyacetylene flame, and the heating is continued until the bath functions on its own.

Induction Heating. The principle of induction heating as used for metal melting can also be applied in heat treating of ferrous and non-ferrous metals. The equipment is essentially like that described on page 426, except that the furnace or induction coil is open at both ends so that objects can be passed through it. Heat is generated in the outer surface and penetrates to the interior if sufficient time is allowed. The process lends itself especially to surface hardening.²³ Time cycles of only

²² W. Kroll, *Trans. Electrochem. Soc.*, **79**, 199 (1941).

²³ H. B. Osborn, Jr., *Trans. Electrochem. Soc.*, **79**, 215 (1941).

a few seconds are maintained by automatic regulation of power and split-second heating and quenching intervals.

High-Frequency Electrostatic Heating. High-frequency electrostatic heating is finding considerable application in the heating of non-conducting materials. Its chief application at present is in the manufacture of

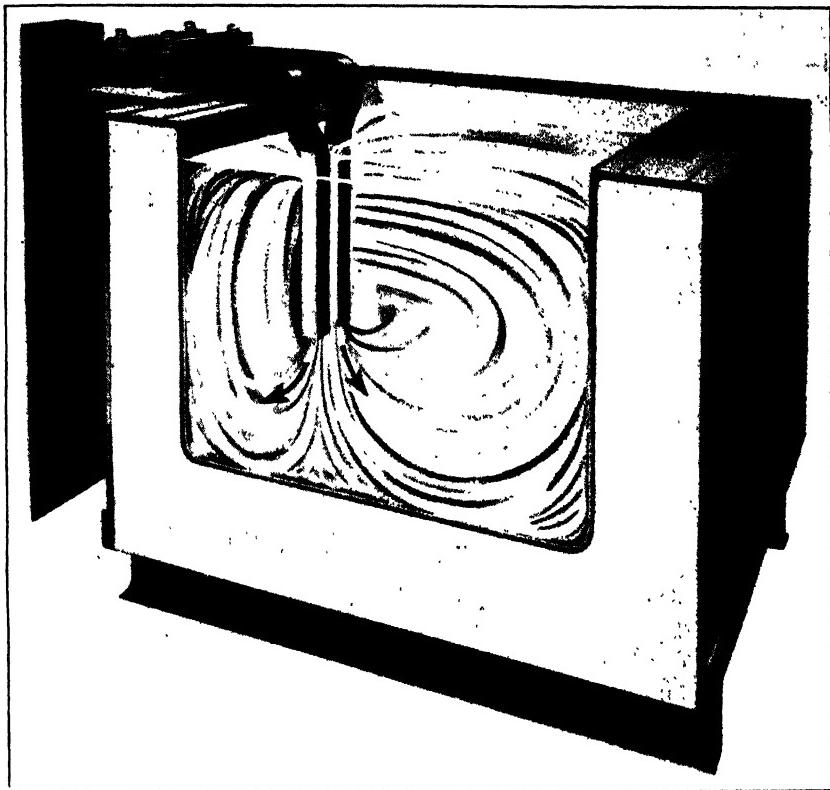


FIG. 212. An Ajax-Hultgren salt bath furnace. (*Courtesy Ajax Electric Company, Inc.*)

plywood to replace the hot plate press, but many other applications are possible.

The theory of the heating process is not easy to present in simple terms, but the process can be described as a distortion of each molecule, first in one direction, then in the other, with each reversal of voltage. This causes internal friction and produces heat in each molecule of the substance. The higher the frequency, the greater the heating effect. Frequencies used are determined by the application of the equipment and may vary from 1 to 10 megacycles. The principle of high-frequency

heating is not new; it has been used for years by doctors to produce artificial fever in patients.

The apparatus, shown diagrammatically in Fig. 213, is similar in some respects to a giant radio set. The heat is generated in the object itself so that problems of heat transfer in poorly conducting materials are absent. In addition to the manufacture of plywood the process has been applied successfully for the drying of tobacco in hogsheads, the drying of paper, textiles, and powders, the heating of thermosetting plastics, curing

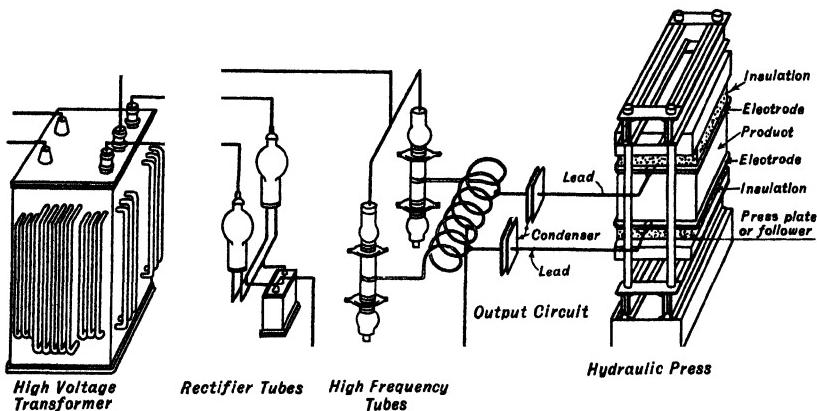


FIG. 213. Power flow diagram of Thermex high-frequency electrostatic heating system. (Courtesy *The Girdler Corporation*.)

rubber, gluing, and for the destruction of infestation in grains and cereals. The possibilities are very large, and a large number of additional applications may well be expected.

ELECTRIC FURNACES IN CERAMIC PROCESSES

Resistance Furnaces in Ceramics. Electric resistance furnaces have found considerable application for firing vitreous enamels. The temperature requirements are not high, practically always being below 1,000° C. (1,832° F.). The success of an electric kiln for firing enameled ware is dependent upon three major factors:²⁴ adequate heat insulation, a low temperature gradient between the heating element and the surrounding material, and proper distribution of the heat within the enclosure. To this should be added the importance of a clean kiln atmosphere. Infusorial earth between the inner and outer walls provides good heat insulation. It is desirable that the heating elements, usually a nickel-chromium alloy, encompass the entire arch and that

²⁴ H. E. Kennedy, *Chem. & Met. Eng.*, 30, 219 (1924).

means be provided for heating the floor, in order to obtain good heat distribution. In some furnaces, however, circulating air within the kiln permits placing the resistors at more concentrated areas. To avoid accident to the operator a low-voltage circuit is desirable, but by proper design 250 volts and higher are used without danger.

Operating data have been given by Stansel and Kjolseth.²⁵ A batch resistor furnace, with a heating chamber 12 ft. long, 4 ft. wide, and 18 in.



FIG. 214. Electric enameling furnace, 350/450 kw. (*Courtesy General Electric Company.*)

high, is rated at 260 kw., three phase, 220 volts. The rate of heat loss from the chamber at 830° C. (1,526° F.) with door closed is approximately 21 kw. Operating continuously with 9 to 12 charges of sheet steel per hour, the furnace produced 8 lb. or 3.2 sq. ft. of enameled ware per kw-hr.

A continuous U-shaped resistor furnace for firing enameled ware has been developed by the General Electric Company. The heating chamber is elevated as shown in Fig. 214. The complete furnace consists of an entrance chamber or oven, a preheating chamber for recovery of the heat from the outgoing ware, and the U-shaped heating chamber. The relatively cool incoming ware passes the hot outgoing ware with appreciable heat exchange, thus making the furnace recuperative. The elevation of the floor of the heating chamber is slightly higher than the

²⁵ N. R. Stansel and K. E. Kjolseth, *Gen. Elec. Rev.*, 36, 277-80 (1938).

ceiling of the roof of the entrance chamber, a design feature for reducing the loss of heat from the heating chamber by convection through the entrance and exit openings. The ware is carried through the furnace by a monorail conveyor. One size of furnace is 56 ft. long, 13 ft. wide, and 12 ft. high. It is rated at 300 kw., three phase, 220 volts. The operating efficiency is 8.65 lb. of ware per kw-hr. Rejects amount to approximately 1 per cent.

An electric resistance kiln has been developed for firing decorations on whiteware.²⁶ A decorative kiln operates at about cone 014 (approximately 800° C. or 1,470° F.). Resistors are grids of nickel-chromium, shown in Fig. 210. The kiln is a continuous type and operates on the recuperative principle. The ware is placed on light trays at one end of the kiln, and after it has passed automatically through the kiln on a roller conveyor it is removed at the other end. The tray is then placed on a second conveyor above the first one, and after it is loaded with ware travels through the kiln in the opposite direction. There are, therefore, two continuous streams of ware passing through the kiln in opposite direction. The temperature at the point of greatest heat is 732° C. (1,350° F.).²⁷ The power consumed is approximately 0.8 kw-hr. per dozen of average ware fired. The kiln has three heating zones, with power supplied to each zone at 110 volts single phase, the three zones providing a three-phase load. The total power input to the three zones is approximately 125 kw., and the current to the most highly powered zone is in the neighborhood of 530 amp. A particular advantage of this type of kiln lies in the fact that the most delicate colors can be fired without loss of hue caused by reducing action, because the kiln atmosphere is always oxidizing.

An electric decorating kiln in continuous operation since 1937²⁸ uses nickel-chromium heating elements. The connected load is 94 kw-a. at 220 volts, three phase, 60 cycles. The kiln is approximately 53 ft. long. The ware is carried on a conveyor into the kiln, and after passing through the firing zone it returns at a lower level to the starting end.

Electric resistance car tunnel kilns are used for glost firing²⁹ of whiteware. The temperature requirements are greater than in decoration kilns, and metallic resistors are not used. The kiln is of the recuperative type in which the ware is carried through the furnace on small cars.

²⁶ Anon., *Ceram. Ind.*, 18, 174 (1932).

²⁷ Operating data supplied by R. R. LaPelle, The Electric Furnace Company, Salem, Ohio.

²⁸ Anon., *Ceram. Ind.*, 40, 43 (1943).

²⁹ In glost firing, the glaze previously applied to the ware as a finely powdered form is heated until the fine particles melt and form a thin coating of glaze or glass over the ware.

The kiln has two tracks with cars moving in opposite directions as shown diagrammatically in Fig. 215. There are two heating elements, which consist of a refractory trough or box made of silicon carbide filled with granular graphite. The kiln operates on 700 to 1,000 amp. at 75 to 150 volts. The kiln produces better than 98 per cent first-class ware.

Electric heating is being applied successfully to glass annealing lehrs. Plate glass, optical glass, bottles, fruit jars, and all kinds of hollow glassware require annealing to remove internal strains. The annealing is essentially a slow cooling process. A lehr consists of a long conveyor, fifty to several hundred feet long, enclosed so that as the glassware passes along it is slowly cooled. In order that the cooling may be sufficiently slow, heat must be supplied to the ware in the lehr, generally by gas flames on the inside of the lehr. The maximum temperature near the receiving end of the lehr varies with the nature of the ware, but it is generally from 450 to 600° C. (842 to 1,112° F.), and it gradually tapers off toward the discharge end. Electric heating supplies a special uniform temperature gradient along the conveyor. The temperature can be controlled automatically. The glass annealed in a fuel-heated conveyor may require subsequent washing to remove a light haze formed

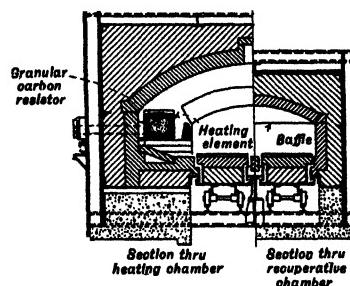


FIG. 215. Section of heating (left) and recuperative (right) chambers of an electric ceramic car tunnel kiln.

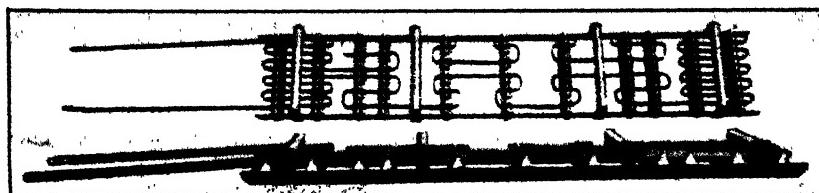


FIG. 216. Resistor heating unit for a glass lehr, 7.5 kw., 55 volts. Frame approximately 4 ft. long. (Courtesy General Electric Company.)

on its surface by the products of combustion in the lehr. With electric heating washing is unnecessary. The heat is supplied by resistors placed preferably under the ware as it passes through the lehr. The resistor unit for a glass lehr is shown in Fig. 216. One bottle manufacturer reported a breakage average of 2 per cent with fuel heat. After changing to electric heating the breakage was reduced to 4 bottles out of 720,000.

Glass-Melting Furnace. Electric glass-melting furnaces have not reached full commercial development but they have been of interest to glass men for many years. The first electric glass-melting furnace appears to have been built in 1905 by Sauvageon. Since then a variety of types and designs have been developed, some of which may have commercial possibilities.³⁰ The heating is supplied by either arc, indirect

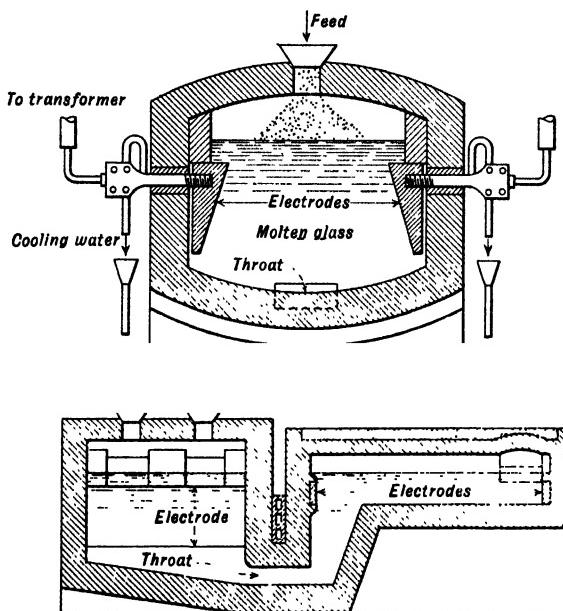


FIG. 217. Electric glass furnace. The molten glass serves as the resistor.

resistance, or direct resistance, in which the molten glass serves as the resistor, or by a combination of the last two.

An arc furnace has been designed by Maetz of Sweden, who built a bridge wall below the arc so that no carbon particles could reach the glass. He melted glass with an expenditure of 0.6-to 0.9 kw-hr. per lb. of product.

Glass appears to become an ionic conductor at above 200° C. (392° F.). Its conductivity increases rapidly with rise in temperature, doubling for about each 200° C. rise in temperature, reaching a specific value of 0.4 ohm-cm. at 1,400° C. (2,552° F.). One type of resistance furnace, developed by Raeder, is shown in Fig. 217. Graphite electrodes are used,

³⁰ Described by J. Horowitz, in a series of articles in *Glashütte* in 1934, translated by S. R. Scholes, *Glass Ind.*, 15, 62, 159 (1934).

but impurities in the graphite and the reducing effect of carbon and carbon monoxide are important factors. With very pure graphite electrodes, glass can be produced free from defects. Raeder used three-phase alternating current led into the glass through three pairs of electrodes, placed entirely beneath the glass bath on opposite sides in the tank. A small throat led the glass from the melting to the refining chamber, where one pair of electrodes was placed. The glass made good bottles, and the power consumption of 200 to 250 kw. continuously on a tank rated at 5 tons daily amounted to about 0.5 kw-hr. per lb. The electrodes were large in order to reduce the current density to 3 to 9 amp. per sq. cm.

For independent resistor furnaces none of the commercially available metallic resistors can be used above 1,300° C. (2,372° F.). Granular carbon and special silicon carbide resistors such as "Globar," "Silit," and "Quartzit" have proved successful. Resistors in the form of sheets or strips have been found practicable for temperatures up to 1,400° C. (2,552° F.). Indirect resistance heating offers the advantage that no special precautions need to be taken against discoloration of the glass. The heat is transmitted to the glass entirely by radiation. The furnaces are usually pot furnaces with resistor rods placed below and above the pots. Radiation is so rapid that in practice resistors are only 50° C. (90° F.) hotter than the glass. The time necessary to melt and prepare a pot of glass can be cut to 11 hr., in comparison with 15 hr. for gas heating.

An electric glass melting furnace so designed that it may be used for the manufacture of glass wool has been developed in the United States.³¹

High-Frequency Electric Glass Welding. High-frequency glass welding is still in the experimental stage although it is used to some extent on a production basis.³² At ordinary temperatures glasses are insulators, but at elevated temperatures they become electrolytic conductors. The welding process, unlike that of metal welding, usually requires high voltages and high frequencies. The voltages and frequencies most suitable depend on the kind of glass, type of ware, and nature of the operations. In some cases ultra-high frequency is most desirable; voltages range from 400 to 100,000 volts.

The electric welding is used in connection with flame heating. In one type of operation the gas burner serves as one electrode and a carbon rod serves as the other. The glass to be heated is placed between the electrodes, the gas flame strikes one side of the glass and as soon as the

³¹ H. F. Hitner (Pittsburgh Plate Glass Company), Electric glass melting furnace, U. S. Patent 2,122,469; *Ceram. Ind.*, 31, 42 (1938).

³² E. M. Guyer, *Trans. Electrochem. Soc.*, 79, 187 (1941).

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glass becomes sufficiently hot an arc or ion flame plays between the carbon electrode and the hot glass, completing the heating operation in a few seconds.

The principal advantages of electric glass welding in production operations are faster melting, deeper heat penetration into thick glasses, and more accurate control of the glass temperature.

CHAPTER XVIII

ELECTRONICS

When electricity passes through gases many new phenomena present themselves which do not exist for metallic or for electrolytic conduction. Only in a few exceptions is Ohm's law valid. The gas particles are in rapid motion; some are charged, others are neutral. When a sufficiently large potential is applied between terminals in a gaseous medium, charged particles are formed, some particles drift slowly, others rapidly, and collision of oppositely charged particles frequently results in the formation of neutral particles. Furthermore, the electrical conductivity changes markedly with variations in pressure of the gas.

Ionization of Gases. A gas, such as air, is a very poor conductor of electricity unless an extremely high potential is applied. Under ordinary circumstances thousands of volts are required to break down the resistance. When this does happen, there is a great surge of electricity accompanied by a brilliant flash of light. The potential required to cause sparking depends upon the shape of the electrodes, their distance apart, and the nature and pressure of the gas between them. This phenomenon therefore offers a means of measuring high potentials in terms of the length of a spark gap. The relation between voltage and spark gap is shown in Table XXXI.¹

It is generally assumed that the conductance of electricity by gases is due to the breaking up of the gas into positively and negatively charged particles which are called gaseous ions. These ions consist of electrons or of atoms or molecules which have gained or lost one or more electrons.

A gas may be made conducting, i.e., it may be ionized, by several methods. Such ionizing agents may be high temperatures; certain chemical reactions; cathode rays; the α , β , and γ radiations emitted by radioactive substances; and the action of X-rays and of ultraviolet light.

¹ Taken with permission from J. B. Hoag, *Electron Physics*, p. 188, D. Van Nostrand Company, New York, 1929.

TABLE XXXI

SPARKING POTENTIALS

Voltages required to just break down non-ionized air at 760 mm. pressure and at 25° C. Electrodes ungrounded

Spark Gap, cm.	Kilovolts Required to Produce a Spark			
	Between needle points	Between 1-cm. spheres	Between 12.5-cm. spheres	Between 25-cm. spheres
0.25	3	10	9	
0.50	5	17	17	
1.00	12	27	33	
1.50	17	32	45	
2.0	23	36	59	60
4.0	42	45	109	91
6.0	56		151	163
8.0	66		185	206
10.0	75		214	245
20.0				392
30.0				480

HOT-CATHODE OR THERMIONIC TUBES

Thermionic Emission. A hot body will emit electrons at a temperature usually far lower than that required to volatilize appreciably any of the metal itself. The thermionic emission of electrons may be considered an evaporation of electrons from the surface of an electrode in much the same way as water molecules are evaporated from the surface of water by the application of heat. As a matter of fact, this phenomenon of boiling electrons out of a metallic surface obeys similar thermodynamic laws. However, there is the important difference that after the electrons have left the surface of the metal there is a mutual repulsion between the negatively charged electrons. The metal, therefore, soon becomes surrounded by a cloud of electrons which will repel others trying to escape from its surface. This phenomenon is commonly known as the space charge. If now a positive potential is applied to another electrode placed near by, some of these electrons will be drawn away from the hot electrode and a space current of electrons will be set up between the two electrodes. The electrode in any such electronic

device which serves as a source of electrons is called the cathode; this also applies to photoelectric cells to be discussed later. The space current will increase with increasing anode potential until the electrons are drawn to the anode as fast as they emerge from the hot cathode surface. This final state is known as emission limitation, and the voltage at which it is reached is known as voltage saturation.

Dushman has shown that the current given out by a hot electrode at any temperature can be represented by the following equation:

$I = \text{saturation current per sq. cm.}$
of the surface of the hot electrode

$$I = aT^2 e^{-b/T}$$

a and b = constants of the emitting surface; for tungsten, $a = 60.2$, $b = 52,400$

T = absolute temperature, °K.

e = Napierian base = 2.71828

This phenomenon of thermionic emission has been utilized for producing tubes of suitable construction which have become of great importance in radio work and other applications, such as rectification, amplification, oscillation generation, and a variety of others. The thermionic tube in its simplest concept will be briefly discussed. For a fuller treatment the reader is referred to various books on the subject.²

Thermionic Rectifier. A schematic presentation of a simple thermionic rectifying tube appears in Fig. 218. The hot filament (cathode)

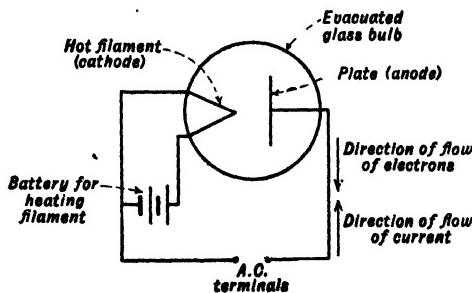


FIG. 218. Thermionic rectification tube.

is heated by a battery as shown, and a cloud of electrons is emitted which forms around the cathode. If a source of alternating current is

² R. G. Kloeffer, *Principles of Electronics*, John Wiley & Sons, New York, 1942; J. H. Morecroft, *Electron Tubes and Their Applications*, John Wiley & Sons, New York, 1933; R. G. Hudson, *Electronics*, John Wiley & Sons, New York, 1932; L. R. Koller, *The Physics of Electron Tubes*, McGraw-Hill Book Company, New York, 1934.

applied to the terminals and the direction of the voltage is such as to help force more electrons out of the cathode, a large number will move to the anode and "condense" on the surface. The passage of the electrons across this space is augmented by the fact that during this same half cycle electrons have been drawn out of the anode and away along the wire, by the pull of the voltage, so that the electrons in the cloud are being attracted by the anode. Another way of stating this is that, during this half-cycle, the hot cathode is made negative, the anode positive, by the alternating current, the voltage drop set up between the electrodes draws the electrons in the cloud over to the anode, and thus there is a passage of current across the space between electrodes.

During the other half of the cycle the hot filament still tends to send out its cloud of electrons, but the voltage of the circuit is reversed and tends to oppose this action; the outside voltage tries to force electrons out of the anode, across the space and onto the cathode, and thus destroy the cloud formed around the hot cathode. As long as the voltage is insufficient to accomplish this reversal, no current will flow during this half-cycle. The tube therefore acts as a half-wave rectifier. By properly connecting two tubes with the secondary of a transformer, full wave rectification will be obtained.

The amount of thermionic current obtained between the electrodes depends upon a number of factors such as the nature of the emitting surface on the cathode, its temperature, and the nature and pressure of any surrounding gases. A slight increase in operating temperature will increase the efficiency of emission at the expense of the expected life. At a certain condition of operation a thoriated-tungsten emitter will give approximately 1 amp. of useful emitted current per sq. cm. of surface. Under similar conditions the oxide-coated emitter will give only 0.1 amp. or less of useful current. This would lead to the conclusion that thoriated tungsten was more desirable, but it requires over 20 watts energy per sq. cm. for operation, whereas the oxide-coated emitter requires only 2.2 watts per sq. cm.³

Tungsten is the most commonly used metallic emitter. It has a high melting point and can be operated for thousands of hours at a temperature high enough to furnish a satisfactory supply of electrons, but its efficiency as measured in amperes of emission per watt is relatively low. It was formerly used in all kinds of electron tubes; its chief present-day use is in tubes having a high plate voltage and wherever positive-ion bombardment of the cathode is likely to occur. It is used for cathodes in tubes with ratings from 1 kw. up and plate potentials of 4,000 volts and higher.

The thoriated-tungsten cathode is made of pure tungsten impregnated with a little thorium oxide and carbon. At its normal operating temperature of 2,000° K. it has an emission of more than 10,000 times that of tungsten at the same temperature. However, tungsten can be used at 2,400° K., but even then thoriated tungsten has 90 times the emission at its lower working temperature. The use of the thoriated-tungsten cathode is at present limited to small power-amplifier tubes, with capacities from 100 to 1,000 watts and plate voltages up to 4,000 volts.

A widely used emitter material consists of a nickel alloy coated with barium oxide or strontium oxide or a mixture of the two. The oxide coat is used largely in the heater-type cathode, which consists of a small metal tube having an oxide coating on the outside and a tungsten filament on the inside for heating the tube to the proper temperature of approximately 900° K. It is used for service up to 100 watts and with plate ratings up to 600 volts. It is used in millions of tubes in alternating-current receiving sets.

The electrodes are mounted in a glass or metal container usually called a tube. This container may be highly evacuated (10^{-8} atm.) or it may contain an inert gas or vapor, such as argon or mercury vapor. The tubes are called vacuum tubes and gas-filled tubes respectively, although in popular usage both types are commonly called vacuum tubes.

In the vacuum tube the current is limited entirely to the electrons emitted from the hot cathode. The vacuum two-electrode tube has a relatively low current rating and a high potential drop from anode to cathode. It will stand a high inverse voltage without an arc-back. It is little used as a low-voltage rectifier but finds application where high voltages are encountered, such as furnishing 10,000 to 100,000 volts direct current for X-ray machines and electrostatic precipitators. The Kenotron rectifier described below belongs to this class.

The gas-filled two-electrode tube will conduct much larger currents than the same tube under a vacuum. Gaseous ions are formed; negative ions serve as carriers of electrons to the anode, and the positive ions tend to neutralize the effect of the space charge. The gas pressure varies from 10^{-5} atm. to several pounds per square inch, depending upon the service for which the tube is designed. Argon or mercury vapor are most commonly used for this purpose. A gas-filled tube has a lower potential drop across the electrodes than the vacuum tube. The Tungar and Rectigon rectifiers described below belong to this class.

Formerly a source of direct current was employed for heating the filament as illustrated in Fig. 218, but since the demand has arisen for filaments of greater total electron emission and therefore more power consumption, the practice has developed of heating the filament with

alternating current supplied from a step-down transformer. Figure 219 illustrates how full-wave rectification is obtained with one tube with two plates.

The thermionic rectifying tube, also called a thermionic valve, two-electrode tube, or diode, is a member of the larger class of tubes called vacuum tubes and electron tubes.

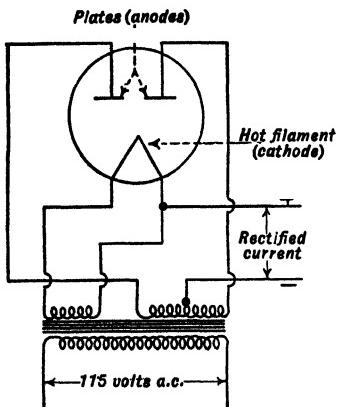
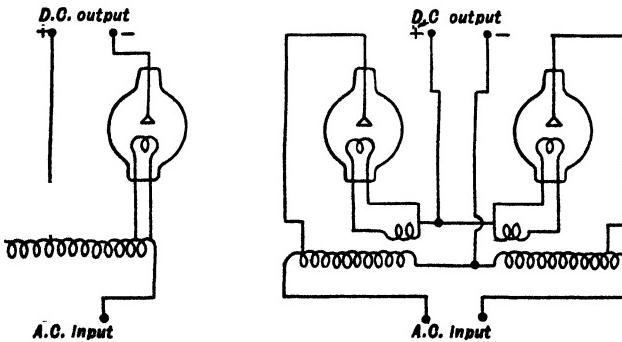


FIG. 219. Thermionic full-wave rectifier.

One type of commercial thermionic rectifier is the *Kenotron*. The filament may be made of pure tungsten or of a nickel alloy coated with certain salts. Its particular usefulness is in the field of high voltages, as for rectification in connection with electrostatic precipitation of dust and fumes. Owing to the small mass of electrons which the Kenotron uses for the conduction of current, the tubes are very rapid in their action, and cleancut rectification of radio frequencies is easily attained with them.

Another type of commercial thermionic rectifier is called a *Tungar* rectifier (General Electric) and a *Rectigon* (Westinghouse). The tube is similar to a Kenotron, but argon is introduced at a pressure of about 70 mm. of mercury at room temperature. The argon greatly reduces



(a) Half-wave rectification.

(b) Full-wave rectification.

FIG. 220. Tungar or Rectigon circuits.

the space-charge drop, but this diminishes the ability to hold back high voltages in the reverse direction. The anode is made of graphite, the cathode of tungsten. When the parts are assembled in the bulb, a ring of magnesium wire is placed around the anode. After the air has

been pumped out of the tube and the argon has been admitted, the tube is sealed off and the anode is heated. The magnesium vaporizes and combines with any traces of air or water vapor which may have been left in the bulb. The excess magnesium continues to absorb impurities throughout the life of the tube. The tube does not respond to as high frequencies as vacuum tubes. If too high a voltage is applied to the Tungar or Rectigon rectifiers, conductance will take place in the reverse direction. There is, therefore, a limit to the voltage at which this type of rectifier will operate satisfactorily, and in the present state of development, completely satisfactory operation cannot be obtained above a few hundred volts. These rectifiers are excellently suited for charging storage cells and for other purposes where low voltage and moderate-amperage direct currents are required. Figure 220 shows two diagrams of this type of rectifier: (a) for half-wave and (b) for full-wave rectification.

The *mercury-arc rectifier*, Fig. 221, consists of a highly evacuated glass bulb or metal chamber equipped with two graphite anodes, a mercury cathode, and an auxiliary anode used only for starting. The anodes are connected to the two terminals of the secondary of a transformer; the primary terminals of the transformer are connected to a single-phase supply circuit. The current can flow through the tube only from either positive electrode to the negative. The tube offers a very high resistance to currents in the opposite direction; thousands of volts would be necessary to reverse the current. The most striking feature of the mercury-arc-rectifier is the manner in which electrons are obtained from the cathode. The cathode consists of a pool of mercury, and the electrons are emitted from a bright spot which moves about on its surface. The passage of the current itself maintains this spot. Before formation of the cathode spot, the rectifier will not conduct current in either direction. If the current is interrupted the spot must be started again; this can be done by means of an auxiliary anode which is brought in contact with the cathode and then removed. By breaking a current passing between the two electrodes a small arc is started and the cathode spot is established.

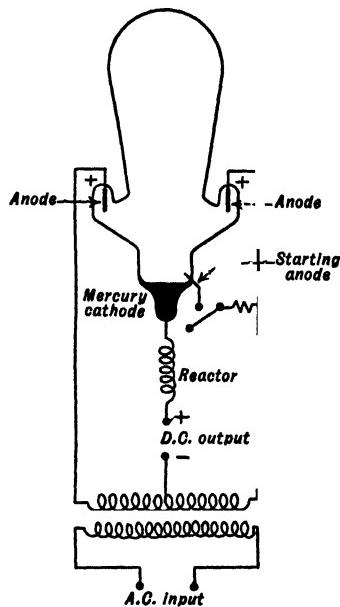


FIG. 221. Circuit of a mercury-arc rectifier.

It is therefore necessary for some current to pass through the rectifier throughout its performance. This makes it necessary to have more than one anode, so that one or the other is carrying a current during each half of the cycle. For small currents the cathode spot becomes unstable, and generally a current of about 5 amp. is required to maintain operation of the rectifier.

Electrons are emitted from the cathode spot. The spot is negative and is bombarded by positive ions. The impact on the spot incr the temperature of the mercury surface where the spot is and thus aids emission of electrons by thermionic means. The theory of the mercury-

arc rectifier is discussed by Prince and Vogdes.⁴ The mercury which is evaporated from the cathode spot is condensed in a chamber immediately above the cathode and runs back again.

Mercury-arc rectifiers find their field of application where moderate voltages and currents are desired. Some of their applications are mentioned in Chapter I.

Thermionic Amplifier. In 1907 deForest found that, by inserting a third electrode into the tube and connecting it properly in the circuit, remarkable voltage amplification could be obtained. A schematic presentation is given in simplified form in Fig. 222.

The third electrode is usually in the form of an open wound wire cylinder; it normally surrounds the filament rather closely and is in turn enveloped by the cylindrical plate. An applied potential of 1 volt to the grid may have many times as much influence on emission as the same potential on the plate. The ratio of change of plate potential to change of grid potential to produce equal changes in the plate current is called the voltage amplification of the tube, or the amplification factor.

The theory and equations involved in amplification are too complex to be discussed in a book of this nature. For fuller information the reader is referred to the references cited above. The application and potentialities of the tube are far-reaching. The tube has found wide use in amplifying weak currents that could not of themselves operate relays, as will be mentioned in the next section on photoelectric cells.

⁴ D. C. Prince and F. B. Vogdes, *Principles of Mercury Arc Rectifiers and Their Circuits*, p. 38, McGraw-Hill Book Company, New York, 1927.

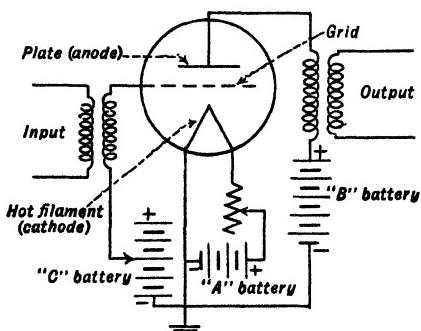


FIG. 222. Thermionic amplification tube.

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⁴ D. C. Prince and F. B. Vogdes, *Principles of Mercury Arc Rectifiers and Their Circuits*, p. 38, McGraw-Hill Book Company, New York, 1927.

DeForest called the device the "Audion," and it was first used as a radio detector. It finds application, to mention some of its uses, as a sensitive voltmeter, sensitive relay, telephone current amplifier, and high-frequency amplifier.

The thermionic amplifier is also called a three-electrode tube, triode, and is a member of the large class of tubes called vacuum tubes and electron tubes.

The addition of a second grid to a three-electrode tube makes possible a further control of the space charges and hence of the plate currents. A tube with two grids is called a tetrode or screen-grid tube. Tubes are in use with as many as five grids.

Three-Electrode Gas-Filled Tubes or Grid-Controlled Tubes. The high-vacuum amplifiers as described above are used in radio receivers but have other applications also. Tubes of this type have been developed to carry several hundred milliamperes. The comparatively small capacity of these tubes does not bring them into the class of power apparatus, although they serve a very useful purpose in sensitive circuits, as linear amplifiers and as accessories to high-power tubes.

Within the last few years many types and sizes of grid-controlled gas and vapor tubes (in distinction to vacuum grid-controlled tubes) have been introduced under such trade names as Grid-Glow (Westinghouse), and Thyratron (General Electric). These tubes utilize a gas or vapor (mercury vapor is most common) which ionizes under impact by electrons, and the resulting ions reduce the space-charge limitations inherent in high-vacuum tubes. As a result, tubes of this type have been made to carry several hundreds of amperes and are, therefore, power devices. A typical tube contains an oxide-coated cathode which is the electron emitter, an anode which collects the electrons, and a grid which controls the discharge. The Thyratron is made in two types, the inert-gas and the mercury-vapor type. The construction and operation of the two types are similar. The starting of the anode current and also its magnitude may be controlled by a small negative bias applied to the grid.

These tubes can be used not only as rectifiers but also as oscillators for converting direct to alternating current, making it possible, for example, to operate alternating-current equipment from direct-current circuits. Alternating-current radio sets, for instance, are operated from direct-current circuits by the use of grid-controlled tubes.

The Ignitron. The grid-controlled tube has certain cathode limitations. A time delay in starting is essential in order that the cathode shall reach operating temperatures before current is drawn. This delay may be only 2 or 3 seconds for small tubes or as much as an hour

for large ones. The disadvantage of such delay is obvious, and it introduces a serious difficulty in those applications where power interruptions must be avoided, for example, in inverters and rectifiers feeding industrial or domestic power systems. In such instances spare tubes must be kept in readiness in case of tube failure, and to avoid interruptions the cathodes must be kept energized.⁵ Such tubes also have a low overload capacity.

A new method has been described by Slepian and Ludwig⁶ for initiating the cathode of an arc. A crystal of certain materials, such as silicon carbide, is immersed in a mercury pool and a current is passed from the crystal to the mercury. At a definite value of voltage and current, a tiny spark appears at the junction and immediately grows into the cathode spot of an arc. If an anode properly spaced is held at a positive potential with respect to the arc, the arc will transfer to the anode very quickly and the relay or switching action is complete. This whole mechanism may occur in only a few microseconds. The advantages claimed for such a rectifier as compared to the hot-cathode type previously described are absence of delay when put into service, high overload capacity, and longer life. As compared to the mercury-arc rectifier it has less tendency to arc back and does not require the 5 amp. or more in the keep-alive circuit. This type of rectifier has been called the Ignitron.

The Ignitron is of special interest to the electrochemist, for it has become a widely used rectifier for commercial operation,⁷ such as producing direct current for electrorefining cells, aluminum cells, magnesium cells, chlorine-caustic cells, and for power for mine haulage and machinery operation.

The Inverter. The transmission of energy by means of direct current is more efficient than by alternating current at the same effective potential because it is accompanied by less dielectric loss; direct-current transmission is also more stable. It is therefore desirable to convert the high-potential alternating-current power into direct-current power for transmission. The alternating current can be converted to direct current by means of mercury-arc rectifiers, grid-controlled rectifiers, or the Ignitron. At the load end of the line the grid-controlled tube can again be used to convert the direct to alternating current.

This conversion can be accomplished by the typical equipment shown in Fig. 223, called an inverter. If direct current can be made to flow in consecutive and periodic pulses from *D* to *E* alternating with impulses

⁵ D. D. Knowles, *Electronics*, p. 164, 1933.

⁶ J. Slepian and L. R. Ludwig, *Trans. Am. Inst. Elec. Eng.*, **52**, 693 (1933).

⁷ J. H. Cox and D. E. Marshall, *Trans. Electrochem. Soc.*, **72**, 183 (1938); F. L. Kaestle, *ibid.*, **76**, 453 (1939); C. S. Levy, *Chem. & Met. Eng.*, **47**, 344 (1940).

from *D* to *F* in the primary winding of the power transformer, the secondary winding will deliver alternating current.

The periodic and alternate diversion of the direct current from *DE* to *DF* is obtained by means of two grid-control rectifiers, *A* and *B*, a large condenser *C*, and a control transformer. This control transformer is connected to a small source of alternating-current power of the same frequency as that desired from the power transformer, or it may be connected to the secondary winding of the power transformer, in which case proper circuit constants must be introduced to adjust the frequency.

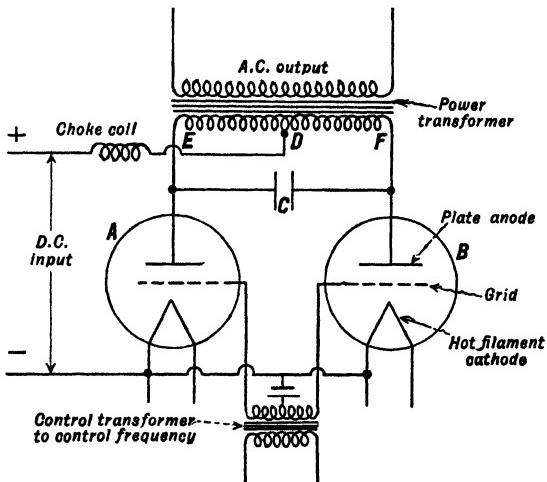


FIG. 223. An inverter for converting direct-current into alternating-current power.

When the control transformer makes the grid potential of rectifier *A* positive with respect to its filament, current will flow from *D* through rectifier *A*. The grid potential of rectifier *B* is now negative with respect to its filament and no current flows through *B*; *F* will, therefore, have about the same potential as *D*. The condenser *C* during this time is charged with its *F* terminal positive, its *E* terminal negative. A reversal of the potential across the secondary winding of the control transformer will reverse the situation, and current will flow from *D* through rectifier *B*.

The reversal of the grid potential of rectifier *A* does not necessarily interrupt its action. It will be observed that the sudden flow of current from *D* to *F* will, in accordance with Lenz's law, induce an e.m.f. tending to send current from *F* to *D*, and the same flux will induce an e.m.f. from *D* to *E*, momentarily lowering the potential of *E*, possibly to a negative value. This reduced voltage of terminal *E* acting with the negative grid of rectifier *A* will stop the flow of current through it.

The condenser is then charged in the opposite direction, and the potential at *E* rises. When the control transformer makes the grid potential of rectifier *A* positive, current will again be conducted through *DE*, and rectifier *B* will be shut off by the process just described for rectifier *A*.

The direct current will, therefore, swing back and forth through the two halves of the primary winding of the power transformer, and alternating-current power will be delivered from its secondary winding and may be transformed to any desired potential. The choke coil in the direct-current line reduces the feed-back of alternating current to the direct-current source.

COPPER OXIDE AND SELENIUM RECTIFIERS

Two useful rectifiers deserve mention here for their action is essentially electronic, although the processes involved are not clearly understood.

The Copper Oxide Rectifier. The copper oxide rectifier⁸ depends upon the fact that a layer of cuprous oxide, Cu₂O, on pure copper has a much higher resistance in one direction than in the other. The element is produced by heating a disc or sheet of copper in air in a furnace to a temperature of approximately 950° C. (1,742° F.) and then quenching in water. This heating produces a layer of cuprous oxide next to the metal and an outer layer of cupric oxide which must be removed.

At the junction between the copper and the oxide, electrons flow readily from the copper to the oxide but not in the reverse direction.

A rectifying unit consists of a copper disc coated on one side with cuprous oxide; a graphite coating and a thin lead washer or coating of electrodeposited nickel are placed on top of this. The whole assembly consists of alternate copper oxide discs and lead washers held together tightly by an insulated bolt passing through a hole in the center of each disc.

Commercial copper oxide rectifiers usually consist of a number of elements combined in series or in parallel. The direct-current volts per disc range from 3 to 20, the higher voltage requiring forced ventilation. The resistance of the rectifier increases slightly with age.

Copper oxide rectifiers are finding application for such services as electroplating, battery charging, motion-picture arcs, and cathodic corrosion protection.

The Selenium Rectifier. The selenium rectifier is similar in operation to the copper oxide rectifier. An iron or aluminum plate is coated on

⁸ L. O. Grondahl, *Trans. Electrochem. Soc.*, **72**, 225 (1937); I. R. Smith, *Westinghouse Engr.*, **3**, 85 (1943).

one side with a layer of selenium which is reduced to metallic conducting selenium in a very thin layer. The selenium is covered with a metallic electrode which creates a barrier layer between the selenium and the electrode. When a voltage is applied, electrons move readily from the electrode to the selenium but not in the reverse direction.

The characteristics and uses of the selenium rectifier are very similar to those of the copper oxide rectifier, and its resistance also increases with age. It has been used in Europe for many years but in this country it is relatively new.

PHOTOELECTRIC CELLS

The preceding part of this chapter discussed the emission of electrons from a hot body and the application of this phenomenon for the production of various useful tubes, such as those used for rectification and amplification of alternating currents. Certain materials have the property of also emitting electrons when subjected to electromagnetic vibrations, as, for instance, when exposed to light. Also, electrolytic cells may be constructed in which an e.m.f. is generated when one of the electrodes or the electrolyte is exposed to illumination. Other substances become conducting when exposed to illumination. All these are the result of what has been called the *photoelectric effect*, which strictly speaking includes any electrical phenomenon which is caused by radiation. Such phenomena may therefore be grouped into three classes: (1) the *photoemissive effect*, the actual liberation of electrons, illustrated by sodium emitting electrons when illuminated; (2) the *photovoltaic effect*, in which a chemical or physical reaction caused by light produces an e.m.f., illustrated by the copper oxide electrolytic cell; and (3) the *photoconductive effect*, in which light produces a change in the ohmic resistance of a substance, illustrated by the behavior of the selenium cell.

These various phenomena are utilized to prepare a group of cells called phototubes, photocells, or photoelectric cells.⁹

Photoemissive Cells. A variety of metals and other materials possess the property of emitting electrons when exposed to electromagnetic radiation. The alkali metals are used most commonly in this type of

⁹ For a more complete discussion of these various types of cells see books on this subject, as, for instance, V. K. Zworykin and E. D. Wilson, *Photocells and Their Application*, John Wiley & Sons, New York, 1934; R. G. Hudson, *Electronics*, John Wiley & Sons, New York, 1932; A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, McGraw-Hill Book Company, New York, 1932; N. R. Campbell and Dorothy Ritchie, *Photoelectric Cells*, Sir Isaac Pitman and Sons, New York, 1929; B. Lange, *Photoelements and Their Application*, Reinhold Publishing Corporation, New York, 1938.

photoelectric cell because they respond more readily to the rays in the visible spectrum.

Sodium, potassium, rubidium, cesium, and other metals have formed the sensitive cathode surface, but cesium is commonly used at present because its color sensitivity in the red end of the spectrum is greater than that of the other alkali metals.¹⁰ Olpin has published curves showing the spectral distribution of composite surfaces. According to these curves, a clean surface of potassium exposed to a trace of sulphur vapor had its sensitivity increased more than 50-fold.

As a great deal of interest has lately been attached to the therapeutic value of ultraviolet radiation and to the art of photochemistry, a demand

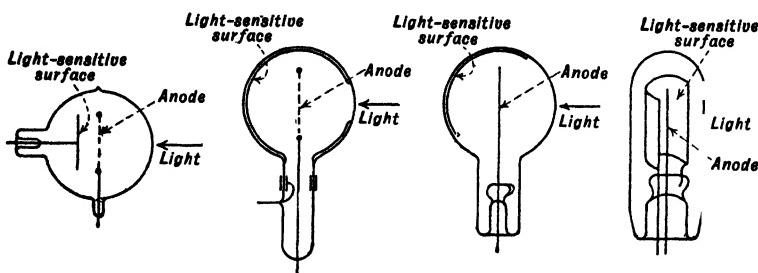


FIG. 224. Typical photoelectric cells.

has arisen for practical cells for measuring the intensity of healthful rays from therapeutic lamps and of photochemical radiations. Rentschler¹¹ found metallic uranium especially suited as the cathode for photoelectric cells for this purpose, especially for short wavelengths down to 2,800 Å. For the region below 3,700 Å, Rentschler suggested the use of thorium; and for the region blue to ultraviolet, the metal cerium. Where response to near ultraviolet but not to the visible is desired, metals like aluminum, zinc, and cadmium are useful. Iron, nickel, and cobalt are suitable where a response only to wavelengths shorter than 3,000 Å is desired. Alkali metals may also be increased in their light sensitivity by subjecting them to a glow discharge in hydrogen and by a variety of other ways that cannot be discussed here.

The cell consists of two electrodes in a glass bulb, or if sensitivity to ultraviolet light is desired, in a quartz or Corex bulb. One of the electrodes, the cathode, is light-sensitive and emits electrons when exposed to light. If a source of potential is applied to the tube to make the cathode negative and the anode positive the electrons are attracted to the anode and a current passes through the cell. Figure 224 shows a

¹⁰ A. R. Olpin, *Bell Lab. Record*, **9**, 310 (1931).

¹¹ H. C. Rentschler, *Trans. Am. Inst. Elec. Engrs.*, **49**, 576 (1930).

number of typical photoelectric cells of the emissive type. The light-sensitive material may be deposited directly on the inside surface of the glass bulb or on another metal. The anode may be a wire, a grid, or a plate (with suitable provision for the light to get to the cathode).

Photoemissive cells are of two general types: the gas-filled and the vacuum types. In both, light liberates electrons from the sensitive cathode. In the vacuum type, this flow of electrons from cathode to anode constitutes the entire current passed by the tube. In the gas-filled tubes, however, the maximum current which can flow is much

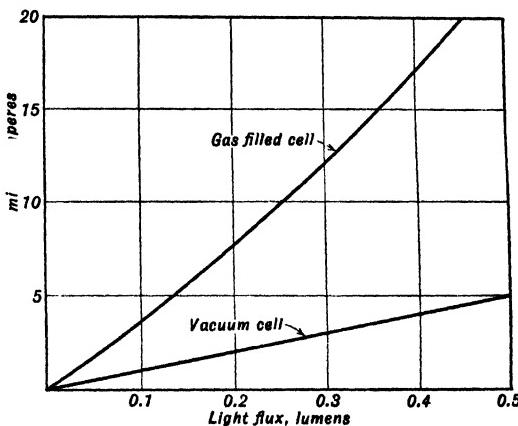


FIG. 225. Anode current characteristics for gas-filled and vacuum-type photoelectric cells.

greater. This is because the electrons, in traveling from the cathode to the anode, collide with atoms of the inert gas in the tube and liberate from the atoms additional electrons which are also attracted to the anode. These electrons collide with other atoms, releasing additional electrons, and so on. This phenomenon, called gas amplification, makes possible the construction of photoelectric tubes capable of passing approximately 10 times the current per unit of light flux that can be passed by vacuum photoelectric tubes. This relation is shown in Fig. 225. The only suitable gases to use are the inert gases, and of these the best is argon, because the increase in current due to ionization by collision is greater than with helium or neon. The inert gas must be highly purified before introduction into the tube, which may be done by subjecting it for several hours to an arc discharge between calcium rods, or to an electron discharge between an incandescent filament and a pool of liquid sodium or potassium. The optimum pressure of an inert gas in a photoelectric tube is of the order of 0.1 mm. mercury.

For vacuum photoelectric tubes the relation between light flux and anode current is linear to a high degree of accuracy. For gas-filled tubes this relation has a slight curvature, but for most purposes it may be considered substantially linear.

Amplification of Photoelectric Currents. The photoemissive current amounts to but a few microamperes,¹² so that it is necessary to amplify this weak current in order for it to operate relays, recording and indicating instruments, and other devices. The most common amplification system uses a three-electrode thermionic amplifier tube (triode) similar to the type employed in radio. The circuit is so arranged that a change in the photoelectric tube current changes the grid voltage of the triode. This causes a proportionate change in the triode plate current, which is of the order of milliamperes,¹³ and may be used to operate relays and other devices. This type of circuit arrangement may be employed on either alternating or direct current.

Some Applications of Photoelectric Cells. By means of suitable relays it is possible for the minute currents furnished by the photoelectric cell to control much larger currents which in turn may be made to operate a large variety of mechanical and electrical devices. Where large amounts of power are to be controlled two or three relays are arranged in series. The current output of a relay may be used to start and stop motors, turn lights on and off, or give an alarm. Anything which produces a change in the light intensity falling on the cell may be made to operate the relay. In this way objects may be counted by their shadows falling on the cell; lights may be turned on or off according to the intensity of the daylight. The cell can be used for opening doors as a person approaches, sorting articles as to size or color, regulating speed of machinery according to whether the feed supply is accumulating or diminishing. The number of devices that can be developed seems to be without limit.

The photoelectric cell is utilized in the construction of color analyzers and color comparators. It has been used as a color indicator and automatic control in chemical titration¹⁴ and to replace the eye in polarimetry. The photoelectric cell has been used as a radiation pyrometer for measuring the temperature of hot bodies¹⁵ and for the measurement of intensities of star images.

¹² One million microamperes (μA) = 1 amp.

¹³ One thousand milliamperes (ma) = 1 amp.

¹⁴ R. H. Muller and H. M. Partridge, *Ind. Eng. Chem.*, **20**, 423 (1928); *J. Sci. Instruments*, **6**, 74 (1929); H. von Halban, *Nature*, **119**, 85 (1927); J. Kenyon, *ibid.*, **117**, 304 (1926).

¹⁵ F. A. Lindemann and T. C. Keeley, *Proc. Phys. Soc. Lond.*, **38**, 69 (1925-26); Research Staff of the General Electric Company, *J. Sci. Instruments*, **2**, 177 (1926).

The largest field of commercial application of photoelectric cells is that of talking pictures. In certain types of talking pictures the sound is recorded photographically on the film in such a way that an exposed

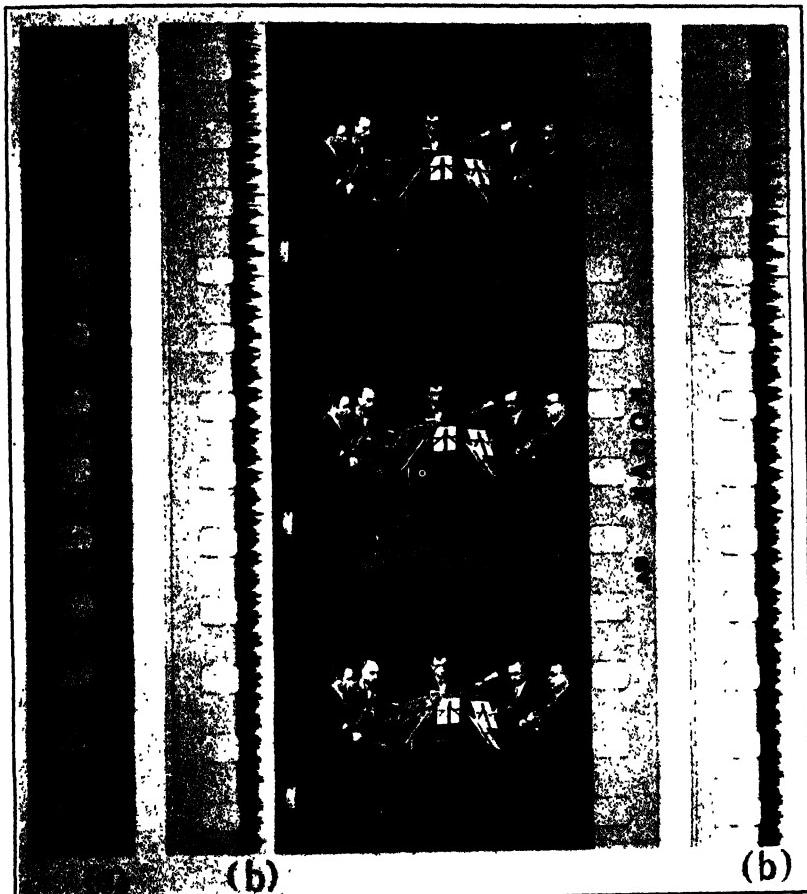


FIG. 226. Motion-picture film with sound record (a) varying in intensity, and (b) varying in width. (*Courtesy Eastman Kodak Company.*)

strip either of variable width or variable density runs along one edge of the film, as shown in Fig. 226. These variations are in accord with the changes in intensity and pitch of the original sound. In the projection machine a strong beam of light passes through a narrow slit and a set of lenses and through the sound record on the film. The light transmitted by the film falls on a photoelectric cell connected to an amplifier and loud-speaker.

Photoelectric cells are also a necessary part of the equipment for television and transmission of pictures

Photoelectric cells find special use in the laboratory for measurement and comparison of light intensities. Because of the linear relation between photoelectric current and light intensity in properly designed cells, one of the first and most widely used applications of the photoelectric effect is in the field of photometry.

Photovoltaic Cells. Photovoltaic cells are cells in which an e.m.f. is generated by the action of light on an electrode or on the electrolyte. The vacuum and gas-filled photoelectric cells discussed in the preceding section require an external source of potential to operate them, but photovoltaic cells require none. They provide their own e.m.f. to drive the current around the circuit.

Photovoltaic cells are of two types, those employing an electrolyte and those that require none. The former may again be divided into two groups, those in which an electrode is sensitive to light and those in which the electrolyte is sensitive to light.

The photovoltaic effect is also called the Becquerel effect, for as early as 1839 Becquerel¹⁶ discovered that, if one of two similar electrodes (platinum or silver, coated with a halide) immersed in dilute sulphuric acid was illuminated, a potential difference was produced between them.

Photovoltaic cells with sensitive electrolytes such as solutions of uranyl or uranous salts are of no practical importance.

Photovoltaic cells with sensitive electrodes are meeting with commercial success. The most common substances used for electrodes are mainly selenium, cuprous oxide, Cu_2O , and to a much lesser extent the silver halides. A simple cell is made up of two copper electrodes similarly coated with cuprous oxide and immersed in almost any electrolyte. Commercially a lead nitrate solution is used. If one electrode is illuminated and the other is not, a voltage is developed within the cell. One commercial type of cell, the Ray-foto, consists of a semicylindrical plate of copper uniformly coated with cuprous oxide. The anode consists of a heavy strip of lead. The cell chamber is a glass cylinder closed at both ends with pieces of Bakelite.

Fink and Alpern¹⁷ have studied this type of photovoltaic cell which consists of the system $Cu : Cu_2O | Pb(NO_3)_2 | Pb$. The electrolyte is a 1 per cent lead nitrate solution. The sensitivity of the cell is .150 ma. per lumen, and the current relation to illumination is linear between 0

¹⁶ E. Becquerel, *Compt. rend.*, **9**, 144,561 (1839).

¹⁷ C. G. Fink and D. K. Alpern, *Trans. Am. Electrochem. Soc.*, **58**, 275 (1930).

and 100 lumens per sq. ft.¹⁸ The cell has a maximum response at about 4,600 Å. It operates successfully in talking-motion-picture projection. It is sensitive over the entire visible spectrum with sufficient current capacity to operate directly a microammeter when used with narrow band-pass filters.

A practical photovoltaic cell that contains no electrolyte has been developed by Lange.¹⁹ It consists of a layer of cuprous oxide on metallic copper. The exposed surface of the oxide is covered with a conducting surface that transmits light. The conducting surface can be prepared by sputtering or evaporating a thin film of metal on the surface of the oxide, or by pressing a grid of wire mesh against the surface. The copper serves as one electrode, the cuprous oxide as the other. The circuit and the direction of flow of electrons are shown in Fig. 227. The yield of the cell is very high, the effect being approximately 10 times as great as that of a good alkali photoelectric cell in a vacuum. The cell, like other photovoltaic cells, generates its own e.m.f. and requires no potential applied externally. This type of cell has been studied by Fink and Fogle.²⁰

A commercial cell of the above type is the Photox (Westinghouse). It consists essentially of a layer of copper oxide, Cu_2O , formed on a disc of copper metal and coated with a transparent film of conducting material. The disc is mounted in a molded case bearing two terminals, one of which is electrically connected to the copper (positive) and the other to the conducting film, which in turn makes contact with the copper oxide (negative). For low external resistance and low illuminations, the current is sensibly proportional to the intensity of light. For low resistance the current output is of the order of 3 μ a. per foot-candle. The voltage output is about 0.25 volt at 10 foot-candles. The color response is very close to that of the human eye, which makes it especially suitable for measuring light intensity. The Photox is capable of operating directly a meter-type relay, or it may be used in conjunction with an amplifier tube for operation of more rugged relays. The cell operates

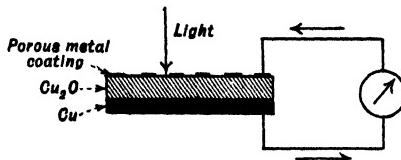


FIG. 227. Copper oxide photovoltaic cell. Arrows show direction of flow of electrons.

¹⁸ If a source of 1 candlepower irradiates a screen at a distance of 1 ft., the intensity of illumination on the screen is said to be 1 *foot-candle*, and the quantity of light that falls per second upon each square foot of the screen is called a *lumen*.

¹⁹ B. Lange, *Physik. Z.*, **31**, 139 (1930).

²⁰ C. G. Fink and M. E. Fogle, *Trans. Electrochem. Soc.*, **66**, 43 (1934).

effectively between temperatures of -50°C . (-58°F .) and 50°C . (122°F .).

Another commercial type of cell using this effect, but with selenium as the light-sensitive material placed on iron, has been called the Photronic cell (Weston). As far as is known, continuous current flow does not harm the cell, and it can be exposed to sunlight without harmful results. It delivers about $120\ \mu\text{a}$. per lumen. The cell has no "dark current," that is, no current flows without the presence of light. It is non-microphonic and instantaneous in its response. Sufficient current is devel-

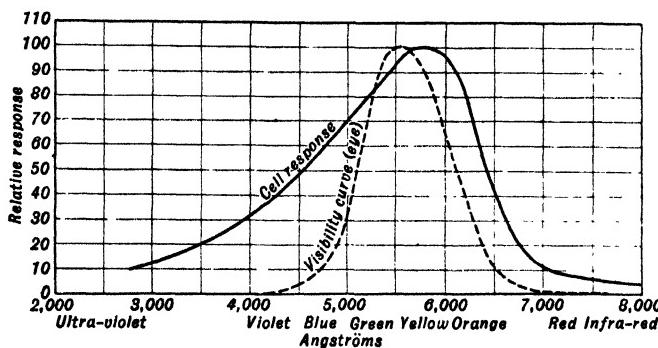


FIG. 228. Spectral response of the Photronic cell. (Courtesy Weston Electrical Instrument Corporation.)

oped to operate relays without any auxiliary apparatus. Figure 228 shows the spectral response of the Photronic cell. A Photronic cell connected to a meter and used as a foot-candle meter is shown in Fig. 229.

Photoconductive Cells. Many substances show an increase in conductance upon exposure to light. This is due to the liberation of electrons within the conductor by the light, but the electrons do not leave the conductor; they remain within it. This effect has been observed in a large number of compounds and some elements. It was first observed in selenium by Willoughby Smith in 1873. Selenium shows the photoconductive effect most strikingly. It exists in several allotrophic forms. If the black vitreous non-conducting form is heated to 180°C . (356°F .) it slowly changes over to the gray crystalline form, which is light-sensitive.

Selenium is a relatively poor conductor of electricity, so that attention has been given to designs that give greater conductivity than do the sticks of the element, in order to obtain the maximum illuminated area with the minimum of resistance. Figure 230 indicates several different methods of attaining this result. Figure 230a shows one of the earlier forms; it consists of two wires wound spirally around an insulator.

Heated selenium is smeared on the surface between the two wires, forming a ribbon of selenium between the wires which act as terminals. In the type shown in Fig. 230b, two closely interpenetrating grids of gold are placed on glass with a thin film of selenium bridging the gaps.

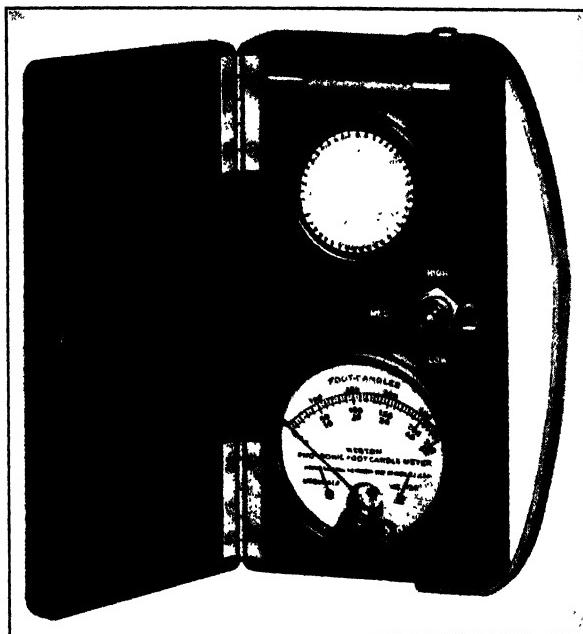


FIG. 229. A foot-candle meter equipped with a Photronic cell. (Courtesy Weston Electrical Instrument Corporation.)

The selenium is distilled onto the glass. Figure 230c shows metal conductors very similar to the two sets of plates of an air condenser. The space between the plates is filled with selenium. All the cells must undergo an annealing process in order to convert the selenium to the

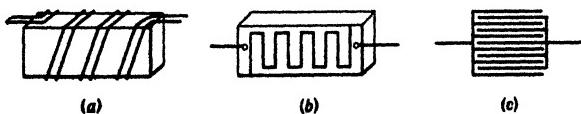


FIG. 230. Types of selenium cell construction.

gray, crystalline, light-sensitive form. In each of the various types, the units are usually sealed in evacuated bulbs with the two wires leading out from the electrodes, or they may be coated with a transparent lacquer.

If a selenium cell is connected in the dark with a source of e.m.f. and an ammeter in series, a relatively low current will be obtained. This is called the *dark current*. If the cell is exposed to light the current increases, not in direct proportion to the illumination but approximately in accordance with the law

$$i = kI^{1/2}$$

where i is the increase in current over the dark current caused by the illumination I , and k is a constant. The photoelectric current is therefore proportional to the square root of the intensity of the illumination. The selenium cell has its maximum sensitivity in red light at about 7,000 Å.

Other substances also show a photoconductive effect. Thallium oxysulphide is sensitive particularly in the infra-red, about 10,000 Å. The Thalofide cell uses this material for its light-sensitive conductor. On account of its sensitivity to the infra-red it may find considerable application for "dark signaling." Cuprous oxide also possesses photoconductivity.

The selenium cell has found widest application of all photoconductive cells. The advantage of this over the photoemissive type of cell is that its current is relatively large so that in many applications relays can be operated without the use of amplifiers. Its disadvantages are its lack of proportionality in response to illumination, its time lag, its large temperature coefficient, and its dark current.

GASEOUS CONDUCTION LAMPS

In recent years there has been considerable development in lamps that contain a gas at a relatively low pressure with the luminosity developed in the gas. They are known under such names as gaseous conduction lamps, gaseous discharge lamps, and gas-glow lamps. The familiar neon signs belong in this class.

When a high-voltage alternating current is applied to the terminals placed in the ends of a tube containing a gas under a definite low pressure, a small current passed through the tube produces a glow. The glow is of a varying color depending upon the gas used.

These lamps are based upon the principle of the well-known Geissler tubes. One of the earliest lamps of this type was the Moore-tube lamp ²¹ introduced in 1894, which contained nitrogen gas. The efficiency was about 7 lumens per watt, and it was necessary to use about 11,000

²¹ D. M. Moore, *Trans. Illum. Eng. Soc.*, 18, 209 (1910).

volts for the lamp, obtained from a step-up transformer located near the lamp. When carbon dioxide was used in the tube the efficiency was about one-half that obtained with nitrogen, but the light was a very close approximation to daylight. At one time these lamps found considerable application in color matching.

In the present-day gaseous lamps for signs, neon is commonly used. The color given by pure neon is an orange red, not suited for general illumination. To obtain the characteristic color of neon the gas must have a high degree of purity. An admixture of 1 per cent of nitrogen will result in radiation completely characterized by that gas. Blue may be obtained by a combination of mercury vapor with neon, and green by a greenish-yellow glass tube with one of the above combinations. The contrast in color makes these signs conspicuous in daylight and even in direct sunlight. According to tests by Cook,²² signs of 12-mm. tubing of an average length of 180 ft. of tubing averaged approximately 8 watts with a power factor of 0.40. Those signs located on a d-c. system were supplied through converters and took nearly 3 times as much power as the a-c. tubes.

Sodium-Vapor Lamps. The neon lamps mentioned above are especially suited for signs and for ornamental lighting but their color precludes their use for general illumination. However, owing to the low energy consumption of gaseous conduction lamps this subject has been a field of extensive research, and much progress has been made, but there will probably be considerable development in the future.

In every gaseous conduction lamp there are a cathode, an anode, and a gas. The electrons emerge at the cathode, and through the influence of the electric potential between the electrodes they acquire a high velocity that causes them to impart energy to the atoms of the gas with the result that the entire gas emits radiations of certain wavelengths.²³ The wavelength is dependent on the nature of the gas. It is therefore desirable to select, if possible, a gas whose radiation is of a wavelength that gives the highest efficiency in the visible range. The maximum sensitivity is at a wavelength of 5,550 Å. By calling this sensitivity 100 per cent, the sensitivity to the eye will give a curve as shown in Fig. 231.²³ Sodium gives a radiation fairly near the maximum visibility, with two wavelengths, $\lambda = 5,890 \text{ \AA}$ and $\lambda = 5,896 \text{ \AA}$, both of which are observed by the eye as one color, thus appearing practically monochromatic.

When a sodium lamp is cold the sodium is solid so that there is practically no vapor. In order to start the discharge, the bulb must con-

²² H. A. Cook, *ibid.*, **24**, 133 (1929).

²³ G. B. Van de Werfhorst, *Trans. Electrochem. Soc.*, **65**, 337 (1934).

tain a gas which has been called an auxiliary gas or filling. Once the discharge has been started with the aid of an auxiliary gas the heat developed must be sufficient to vaporize the sodium, but after the sodium has been vaporized the filling has a decided influence on the generation of light in the sodium vapor. Any one of the rare gases, neon, argon, krypton, and helium, may serve as a filler, but neon is generally chosen for sodium-vapor lamps because it produces more lumens per watt and because the amount of light produced increases with pressure up to 5 mm. whereas that of the others decreases with pressure (except at pressures below 0.7 mm.). The gas is used at a pressure of approximately 2 mm.

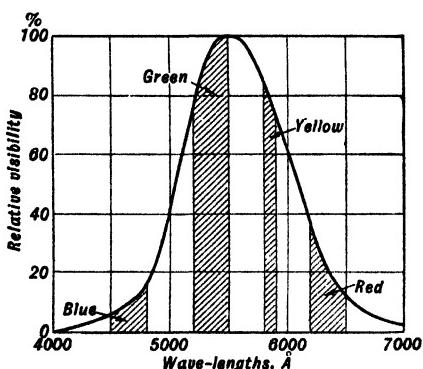


FIG. 231. Relative visibilities of various wavelengths.

Of the various methods available by which the electrons may be made to emerge from the cathode the simplest is to heat the cathode. This may be done by a source essentially independent of the main circuit through the lamp as in the thermionic tubes, or it may be supplied by the energy dissipated by the cathode by the work of forcing electrons from the cathode into the conducting gas.

The former method is more common at present, and oxide-coated filaments like those in thermionic tubes are used.

The lamps may be operated on alternating or direct current. Voltages required for the heating filaments are low, so that when direct current is used the problem of supplying this low-voltage current without appreciable loss is serious; in one type of lamp the heater uses 8 to 10 amp. at 2 volts. The current supplied to the sodium lamps is also of low voltage. In one installation the ignition voltage is 17 volts, the burning voltage 14 volts, for direct current. On account of this low voltage a number of lamps are operated in series. For use with alternating current, lamps have been developed with a burning voltage of 90 volts. A sodium-vapor lamp will give 4,000 to 5,000 lumens per 100 watts as compared to 300 watts for the same number of lumens obtained from incandescent lamps.

In most discharge lamps the voltage characteristic is negative; i.e., the voltage drops with increase in current. Therefore for such lamps the current must be regulated by a resistance or inductance, just as in the electric arc.

With gas discharge lamps the unit surface brightness is low; in sodium-vapor lamps this value is about 10 candles per sq. cm., as compared with 500 candles per sq. cm. for the tungsten-filament lamp. There is little or no glare with sodium lamps so that we have a lamp with high output of light with little surface brightness.

It seems very certain that a few more years will see this type of light source extensively used to supplement the already highly developed incandescent lamp and the mercury arc.²⁴

Fluorescent Lamps.²⁵ Fluorescent lamps are relatively long tubes containing electrodes on the ends; the tubes contain an inert gas at a low pressure and a few drops of mercury. The tube is coated on the inside with a compound capable of absorbing the low-pressure mercury discharge in the ultraviolet at 2,537 Å and radiate this energy in the visible part of the spectrum. In the external circuit is required a transformer, choke coil, or other auxiliary equipment for maintaining the proper operation voltage.

The gas in an unlighted lamp is in an un-ionized condition, and in order that the current may start, the gas must be excited and it must be maintained in this condition during operation. The mercury vapor must be bombarded by electrons having a velocity of several electron volts to excite them. About 6 to 10 volts is required to accelerate electrons at the cathode. There is also a drop of several volts at the anode, so that, in a lamp having a 60-volt drop, 25 per cent of the energy is lost at the electrodes.

One type of electrode consists of a tungsten filament coated with BaO and SrO and is operated hot. In low-current high-voltage lamps the electrodes are cup-shaped and operate without special heating. The electrodes are made of nickel, iron, copper, or nichrome. Several hundred to 1,000 volts is necessary to operate such a lamp.

The inert gas in the tube is most commonly argon at a pressure of about 4 mm. The gas makes starting easier, helps to protect the electrodes against too severe bombardment by the mercury atoms, and adds greatly to the stability of operation of the lamp.

Mercury vapor is required in the lamp at a pressure of a few thousands of a millimeter to give a maximum amount of energy at 2,537 Å.

The tube is lined with one or more fluorescent compounds. Their function is to absorb the one radiation at 2,537 Å which can be produced efficiently with the mercury discharge and to re-radiate this energy in a desirable portion of the visible spectrum. Many compounds fluoresce,

²⁴ L. J. Buttolph, *Trans. Electrochem. Soc.*, **65**, 218 (1934).

²⁵ J. W. Marden, *Chem. & Met. Eng.*, **48**, 80-8 (1941); Staff article, *ibid.*, **48**, 82-8 (1941).

but only a few are suitable for use in lamps. The more common compounds used and the predominant color produced are given in Table XXXII.

TABLE XXXII
COLORS PRODUCED BY FLUORESCENT CHEMICALS

Calcium tungstate	Blue
Magnesium tungstate	Blue-white
Zinc silicate	Green
Zinc beryllium silicate	Yellow-white
Cadmium silicate	Yellow-pink
Cadmium borate	Pink

Some compounds require activators for proper fluorescence; compounds suitable as activators are MnO , PbO , ThO_2 , and others.

The lamp coatings are prepared in ball mills in which the mixture of fluorescent powder and activators is ground with flint pebbles in a mixture of nitrocellulose lacquer and solvents. After a homogeneous mixture is obtained a sample is tested in six lamp tubes, and, if satisfactory, the mix is used for coating tubes in the production line. The coating is applied by automatic equipment in order to obtain uniformity. After coating, the tubes are dried and then fired in a furnace at 388°C ; (730° F.) to oxidize all the organic material in the lacquer.

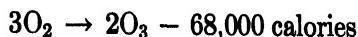
Since impurities in the chemicals, lacquer, or air can easily reduce the efficiency of the lamps elaborate precautions are taken to preserve immaculate cleanliness in the plant.

The electrode assemblies are attached to the tubes, the tubes are evacuated, and the proper amounts of argon and mercury are introduced. The completed lamps are stabilized by lighting for about ten minutes.

CHAPTER XIX

OZONE

Ozone is triatomic oxygen, O_3 , and is formed according to the reaction



The proportion of ozone in equilibrium with oxygen at atmospheric temperatures is low but increases as the temperature rises. It is 0.1 per cent at $1,300^\circ \text{C}$. ($2,372^\circ \text{F}$.); 1 per cent at $4,500^\circ \text{C}$. ($8,130^\circ \text{F}$.). It can be prepared by heating oxygen to a very high temperature and then cooling it suddenly, but the ozone concentration obtained is low owing to the rapid reversion to diatomic oxygen. It can be prepared at much higher concentrations at room temperatures by means of the silent electric discharge. Ozone can also be produced photochemically by the action of ultraviolet light of wavelength of 120 to 180 $m\mu$;¹ but in commercial sources of ultraviolet light the relatively larger proportion of light of greater wavelength (300 to 330 $m\mu$) exerts a decomposing effect on ozone so that the yield is small. Ozone can also be produced by electrolysis of aqueous solutions.

Ozone is produced commercially solely by the silent or brush discharge. There is a close connection between the luminous phenomena observed and the ozone produced; ozone is formed in appreciable amounts only in those regions of the silent discharge which are luminous. It is therefore the practice in some commercial installations to place the ozonizers in a darkened room so that the luminosity is more readily detectable. A large part of the yield of ozone comes from the ultraviolet light accompanying the discharge. In operation, an equilibrium is reached which depends upon the operating conditions such as temperature and pressure; the moisture content of the oxygen or air; the shape, size, distance apart, finish, and age of the electrodes; whether the current is direct or alternating, and if alternating its wave form and frequency.

A greater amount of ozone can be produced per tube with high frequency than with low frequency, on account of the greater absorption of energy, but the energy yield and the concentration of the ozone are not

¹ One million $m\mu$ (millimicrons) = 1 mm.

increased. In practice, frequencies up to 1,000 cycles per second are used. The limiting yield of ozone decreases rapidly as the pressure falls. A rise in temperature rapidly increases the rate of de-ozonization. Nitrogen oxides, chlorine, and water vapor lower the yield of ozone; for a gas with a water-vapor pressure of 7 mm. the yield can easily fall to 60 or 70 per cent of that obtained with the dried gas. An ozonizer consists of two metal electrodes with an air gap and dielectric between; the dielectric usually consists of glass or mica. The nature and thickness of the dielectric have an important bearing on the yield. If no dielectric is used the electrodes cannot be placed close together without fear of sparking. With a dielectric the interpolar distance can be reduced to a far lower figure and the capacity of the ozonizer is increased as well as the yield per kilowatt-hour. Wave form has no pronounced effect. A low current density is used in practice, for any attempt to increase it unduly leads to heat production and poor yields. The yield per ampere-hour increases with increase of voltage up to a certain point, after which there is little change. Voltages up to 25,000 have been used.

When electrical equilibrium has been reached, the ozone decomposes as fast as it is formed, and from then on the yield is not increased. The smaller the ozone concentration the greater the yield, a limiting value in yield being obtained at zero concentration. The yield must therefore be defined in reference to concentration.

For a given ozonizer, the best working conditions are fairly specific and depend upon the relative importance attached to high yield or high ozone concentrations. The optimum voltage, load, and frequency can best be determined empirically, leaving the load factor to take care of itself.

The degree of ionization in an ozonizer is very high so that dust and water vapor present in the air, as they pass through the ozonizer, become charged and are deposited on the electrodes. Myriad minute points will form, from which a sparking discharge instead of a brush discharge takes place. These in turn produce oxides of nitrogen which become absorbed by the deposited water and are ultimately oxidized to nitric acid. The acid attacks the metal parts of the ozonizer. The air passing into an ozonizer is always dried, which is done by refrigeration or by passing it over calcium chloride or silica gel.

On the basis of the heat of reaction there is formed theoretically 1,200 g. ozone per kw-hr. Commercial ozonizers show an efficiency of only about 5 per cent in air and 15 per cent in oxygen.

Siemens and Halske Ozonizer. A commercial unit of this ozonizer is shown in Fig. 232. It consists of an iron box provided with glass windows. A number of vertical glass cylinders pass through the bottom

of the main chamber. Each glass tube is coated on the outside with metal which serves as one electrode. Concentrically inside each tube is placed the other electrode, consisting of a cylinder of sheet aluminum. The air, after drying by calcium chloride, passes along the annular space between the inner electrode and the glass tube. Water is run through the iron box to cool the unit. The inner electrodes are carefully insulated and connected to a source of high-voltage alternating current, which passes from them across the air gaps, through the glass cylinders, and to the iron box, which is grounded.

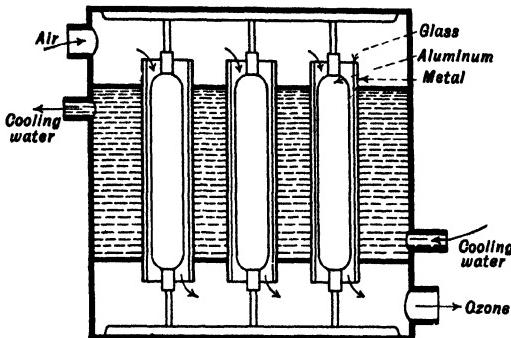


FIG. 232. Siemens and Halske ozonizer.

The voltage varies between 7,000 and 12,000 volts. With a higher potential, insulation troubles are likely to occur. The frequency employed for large installations is generally 500 cycles per second, but smaller units are generally supplied by a 60-cycle transformer.

Under normal conditions, with high frequency, the ozonizer can produce 50 g. ozone per kw-hr. at a concentration of 2.5 g. per cubic meter.

Abraham-Marmier Ozonizer. This ozonizer uses electrodes with plane surfaces with a layer of glass on either side. The electrodes are arranged in parallel rows inside an earthenware casing, the air passing through the spaces between the plates. The electrodes are in the form of metal boxes for easy water cooling, and the flow of water is not continuous but interrupted to avoid short circuiting. The unit operates at 12,000 volts and, owing to the efficient cooling, produces ozone of high concentration.

United States Ozonizer. The United States Ozonizer is manufactured by the United States Ozone Company of America. It has a cylindrical glass dielectric as shown in Fig. 233, so designed that edge discharges are eliminated. An aluminum cylinder encloses the glass tube and forms an annular space around it, through which the air passes. The aluminum cylinder has cast end-pieces provided with inlet and outlet ports. The ozonizers are made to operate on 60 cycles per second where

amounts less than 75 g. per hr. of ozone are required. For larger yields, high-frequency ozonizers are made operating on 1,000 cycles. Ozonizers are constructed in capacities from 5 to 1,000 g. per hr. of ozone. They are built with calcium chloride or silica gel dehydrators. The latter type are equipped for reactifying or regenerating the silica gel by the aid of a small electric heater. The energy consumption of a 20-g.-per-hr.

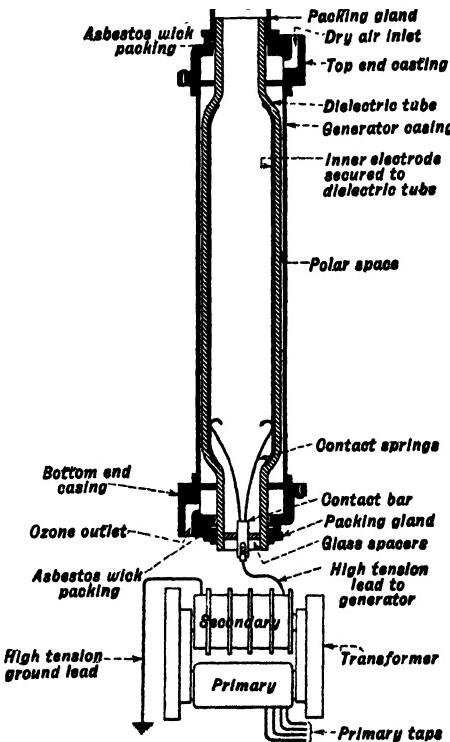


FIG. 233. Sectional view of a U. S. Ozonizer, low-frequency type.

ozonizer is 2.25 kw-hr. per hr., including the electrical energy used for reactifying the silica gel dehydrator. A 1,000-gal.-per-hr. ozonizer with a reactivating silica gel dehydrator is shown in Fig. 234.

Uses of Ozone. Ozone has found a large variety of uses, mainly in the treatment of air and of water.

Ozone has found fairly wide application in connection with ventilation of buildings. It eliminates gaseous impurities by oxidizing them. It destroys malodorous impurities by converting them into non-odorous and harmless forms. In addition, it aids mechanical ventilation systems in removing particles of smoke and other finely suspended contaminants from the air by making them more readily filtrable. Since air contains

appreciable quantities of water vapor which reduces the efficiency of the ozone generators it is not desirable to attempt to treat the whole air in the ozonizer. The United States Ozone Company of America has developed a system whereby a very small part of the air is by-passed to the ozonizer after being completely dried. A high-concentration ozone is produced which is then introduced into the ventilating system and

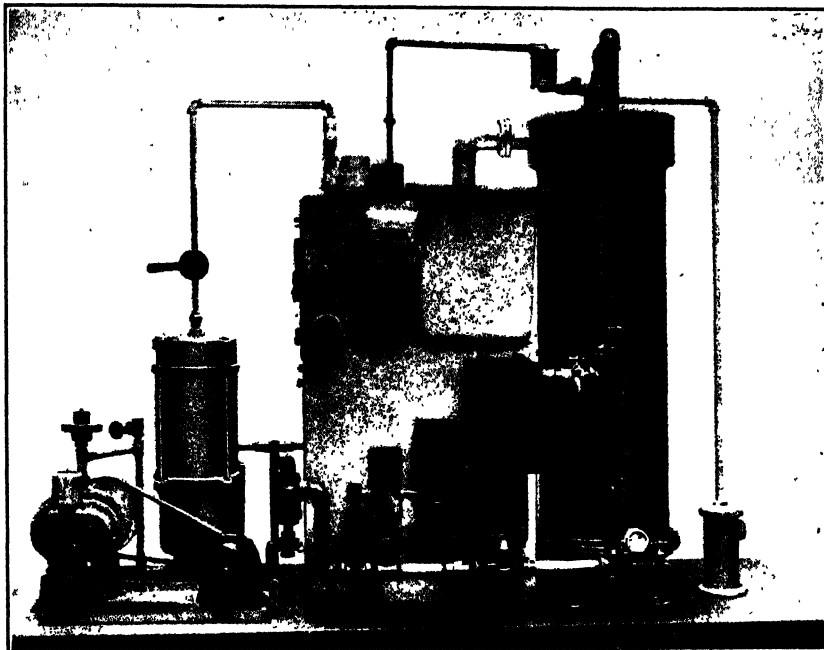


FIG. 234. A 1,000-gallon-per-hour ozonizer and dehydrator. (*Courtesy United States Ozone Company.*)

thoroughly mixed with the air. A concentration of 0.01 p.p.m. (part per million) is recommended for ventilation of public buildings. Ozone in a concentration of 1 p.p.m. gives a noticeable odor and becomes objectionable on constant exposure, and when breathed continuously is dangerous to health. However, tests show a large difference of toxicity between pure ozone and ozone containing nitrogen oxides. The variance of opinion in the literature on ozone toxicity is probably due to ozone containing varying amounts of nitrogen oxides. Ozone free from oxides of nitrogen is non-toxic in concentrations below 20 p.p.m.² For destroying pronounced odors, as in tanneries and egg-sorting rooms, a concentration of 0.1 p.p.m. is necessary.

² C. E. Thorp, *News Ed.*, Am. Chem. Soc., 19, 688 (1941).

Ozone is also used in connection with storage of foodstuffs, such as eggs, vegetables, and meats. For preventing bacterial and fungus growth in meat, egg, and cold-storage rooms a concentration of ozone of 0.5 p.p.m. is necessary.

Another wide use of ozone is in the sterilization of water and in removing undesirable color and taste. When properly applied, ozone destroys all harmful bacteria as well as taste and odor due to excess chlorination, or the introduction of factory wastes such as phenols and cresols, or dissolved organic matter. Ozonizers are used in the United States by a large number of beverage-manufacturing plants and bottlers of drinking water. Water in swimming pools is purified with ozone. It has found very little application for treating of municipal water supplies in this country, but it has long been used for that purpose in Paris³ and in Leningrad,⁴ and such installations have been placed in London and in Paris, where the quantities of water to be ozonized are 15 million and 66 million gallons per day, respectively. The energy consumption for water treatment is from 300 watts per 1,000 gal. for a turbid water down to 150 watts for a clear water.

³ Anon., *Electrochem. Met. Ind.* (now *Chem. & Met. Eng.*), **7**, 411 (1909).

⁴ G. Erlwein, *Z. Elektrochem.*, **17**, 764 (1911).

CHAPTER XX

ATMOSPHERIC NITROGEN FIXATION

Nitrogen is a very important item in the economic life of the world. It is necessary for the perpetuation of plant and animal life, and, almost ironically, it is also an essential component of most of the high explosives and propellants used in modern warfare. But, as pointed out by Curtis,¹ between the extreme roles of fostering life and destroying it, nitrogen plays a most important part in the peaceful arts to which civilization has given rise.

It has been estimated that there are in the earth's atmosphere about 4,000 million million tons of nitrogen, so that it would appear that a shortage of nitrogen would never arise, yet in 1898 Sir William Crookes predicted world starvation unless some new sources of combined nitrogen could be discovered. This is because the atmospheric nitrogen is free, whereas it is useful for sustaining life, in explosives manufacture, and in the industries only in combined form. The problem of "fixing" nitrogen, i.e., causing it to combine with other elements, is therefore vital to mankind.

Natural processes are constantly at work at fixing nitrogen, and until recently man had to rely upon this process for his whole nitrogen supply whether for soil fertility or for industrial uses. A number of processes have been developed for fixing atmospheric nitrogen, some of which are described in this chapter.

FIXATION OF NITROGEN BY ELECTRIC ARCS

From a world viewpoint, the arc method is of minor importance as a factor in the fixation of atmospheric nitrogen. In 1929 the arc process accounted for 15,000 net tons of nitrogen, which was about 1.2 per cent of the total world synthetic nitrogen production; the cyanamide process accounted for about 20 per cent, and the direct synthetic ammonia process for about 79 per cent. At the present time no arc processes are

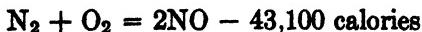
¹ H. A. Curtis, *Fixed Nitrogen*, p. 11, The Chemical Catalog Company, New York, 1932.

in operation in the United States,² and unless new developments are made, the arc process for nitrogen fixation is apparently doomed to disappear from the picture. Arc processes are in use at present in Norway. Those plants that were in operation in the United States were highly localized at places where electrical energy was cheap. The capital investment per ton of fixed nitrogen per year is approximately \$450, which compares unfavorably with other fixation methods. The operating efficiency of energy utilization is also low, being about 65,000 kw-hr. per metric ton of nitrogen. The gases leaving the furnace average approximately 1.2 per cent nitric oxide, so that it is necessary to handle about 175 tons of this gas mixture to obtain 1 ton of nitrogen fixed as nitric acid.

Yet the arc method possesses certain inherent features that set it apart by itself and make it an interesting field of investigation. It uses the fewest, cheapest, and most plentiful of raw materials, namely, nitrogen and water, and produces fixed nitrogen directly in a highly desirable form.

The formation of nitrogen oxides at a high-tension arc discharge in air is the basis of the arc process for fixation of atmospheric nitrogen. It was first recognized by Cavendish,³ but the early experiments were of no industrial significance at the time, since practical means for generating electrical energy in large quantities were unknown. Sir William Crookes and Lord Rayleigh⁴ contributed to further study of this work. The earliest attempt to establish a commercial process was that of Bradley and Lovejoy at Niagara Falls, New York, in 1902.

When air is subjected to a high-tension arc discharge, nitric oxide is formed according to the reaction



At low temperatures nitric oxide, NO, is unstable, its equilibrium concentration in the presence of nitrogen and oxygen being very small. According to the above reaction, high temperatures should favor the formation of nitric oxide, provided that the reaction is strictly a thermal one. That is, the air is heated to the temperature of the arc, and nitric oxide is produced at a definite concentration in equilibrium with nitrogen and oxygen at the arc temperature. As the gases pass out of the arc zone they are cooled, during which time there is a tendency for the nitric

² The La Grande, Washington, plant of the American Nitrogen Products Company of Seattle, the only commercial arc-nitrogen plant of importance ever to be built in the United States, destroyed by fire in 1925 and not rebuilt, is described by E. A. Leow and W. L. Beuschlein, Univ. of Wash. Eng. Exp. Station Bull. 73 (1933). Various arc processes are described by H. J. Creighton, *J. Franklin Inst.*, 187, 377, 599, 705 (1919).

³ H. Cavendish, *Trans. Roy. Soc., London, A* 75, 372 (1785).

⁴ Lord Rayleigh, *J. Chem. Soc.*, 71, 181 (1897).

oxide to decompose to a concentration in equilibrium with nitrogen and oxygen at the lower temperatures. It was therefore considered advantageous to have a high arc temperature followed by very rapid cooling of the gases. However, it was shown by Haber and Koenig⁵ that electrical phenomena can be of greater importance than thermal effects in determining the yield of nitric oxide. It has been suggested by Steinmetz⁶ that the formation of nitric oxide is due to the combination of nitrogen and oxygen atoms which were produced by dissociation in the powerful electric field in the arc, rather than by thermal dissociation.

In the earlier designs of nitrogen-fixation furnaces attempts were made to obtain very high temperatures in the arc with sudden cooling. But it was found that the nitric oxide concentration did not increase at the same rate as the consumption of electrical energy, and that a limit was reached beyond which an increase in energy consumption was useless. As a consequence, highly concentrated arcs were avoided and attempts were made to obtain long stable arcs so that a large quantity of air could be brought in contact with them.

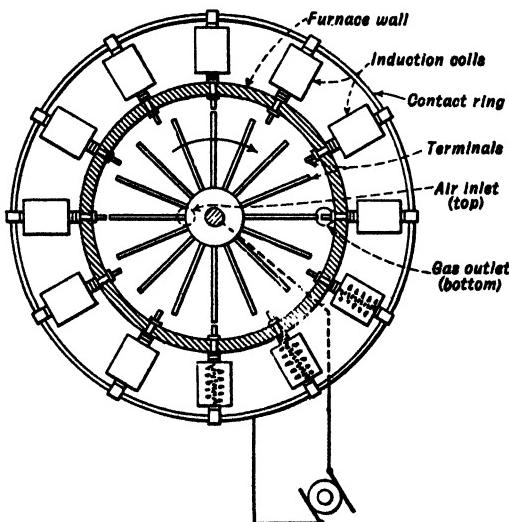


FIG. 235. Sectional plan, Bradley-Lovejoy furnace.

Bradley-Lovejoy Process. The Bradley and Lovejoy process was patented in 1901 and a fairly large plant was built at Niagara Falls, New York, in 1902, but was closed in 1904. The process used a high-voltage direct current, interrupted mechanically. There were 185 arc contacts,

⁵ F. Haber and A. Koenig, *Z. Elektrochem.*, **13**, 725 (1907); **14**, 689 (1908); F. Haber and E. Platou, *ibid.*, **16**, 798 (1910).

⁶ C. P. Steinmetz, *Chem. & Met. Eng.*, **22**, 299, 353, 411, 455 (1920).

and each arc was formed and broken 50 times per second. The unit operated at 0.75 amp. at 8,000 volts, each arc consuming 1 ma.

The air was dried over calcium chloride and was heated before it passed into the apparatus. The hot gases leaving the unit were conducted into an iron reservoir and then into an absorption tower where the nitrogen oxides were dissolved by water or sodium hydroxide solution. One pound of nitric acid was obtained per 7 hp-hr. Figure 235 shows a diagram of the Bradley and Lovejoy furnace.⁷

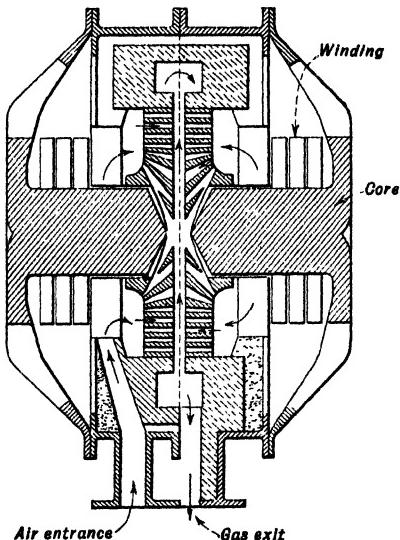


FIG. 236. Sectional elevation of a Birkeland-Eyde furnace at right angles to the arc disc.

disc of flame 6 ft. in diameter at right angles to the line joining the poles of the magnet.

The air enters through perforations in the flat sides, passes through the space containing the arc, and leaves through openings in the circumference of the arc space. The gases from the furnace contain about 1.2 per cent nitric oxide.

A unit takes a current of about 200 amp. at 5,000 volts. The power factor is 0.8. The electrodes last 400 to 500 hr. and can be changed rapidly.⁸

Schönherr-Hessberger Process. This process, also called the Schönherr process,⁹ was developed about the same time as the Birkeland-

⁷ The first installation of the Bradley-Lovejoy process is described by A. Wiesler, *Z. angew. Chem.*, **17**, 1713 (1904).

⁸ A technical unit of the Birkeland-Eyde process is described by K. Birkeland, *Trans. Faraday Soc.*, **2**, 98 (1906).

⁹ Schönherr, *Trans. Am. Electrochem. Soc.*, **16**, 131 (1909).

Eyde process, but instead of a large flame arc it uses a long filament arc. The Schönher unit consists of four concentric vertical tubes as shown in Fig. 237, so arranged that the incoming air is preheated by the outgoing gases. A long, steady arc is produced in the inner tube or reaction chamber. The arc is formed between an insulated electrode near the lower end and the water-cooled upper end of the tube. The air entering the arc chamber is given a rapid spiral motion as it enters through tangential openings. The long narrow arc, in some furnaces 20 ft. in length, assumes a central position in the tube by virtue of this spiral air motion. The inner tube is only 6 or 8 in. in diameter, but the circulation of the air around it keeps it sufficiently cool.

The arc is formed between the tube and insulated electrode by a special rod which can be made to touch both simultaneously and can then be quickly removed. The spiral air currents then cause the arc to travel to the upper water-cooled end of the tube.

The power input may be as high as 1,000 kw. The furnace gases have a temperature of about $1,200^{\circ}$ C. ($2,192^{\circ}$ F.) as they leave the reaction chamber. The concentration of nitric oxide is about 1.8 per cent, which is higher than that obtained in the Birkeland-Eyde furnaces, but the yield is about the same.

Pauling Process. In the Pauling process¹⁰ the arc is formed between two electrodes so shaped and arranged that they make a V-shaped arc gap as shown in Fig. 238. The electrodes are hollow, water-cooled, cast-steel or aluminum tubes set about 2 in. apart at their base and about 3 ft. at the top. They are provided with vertical slits at the base through which thin steel blades pass, and whose distance apart can be regulated. These blades are used for starting the arc and are so thin that they do not interfere with the flow of air from the nozzle beneath. As soon as the arc is formed the air blast blows it along the divergent electrodes until it is broken, after which a new arc forms. The arc has the appearance of a vertical sheet of flame. The life is about 200 working hours for the main electrodes and 20 hours for the starting electrodes.

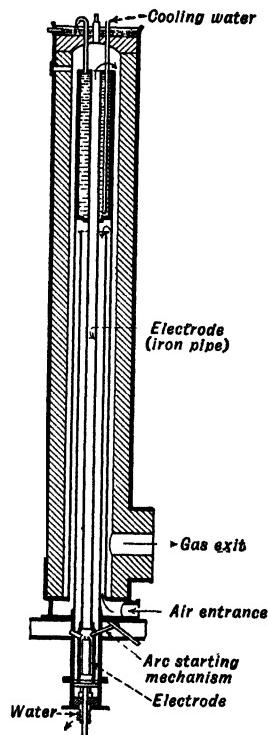


FIG. 237. Schönher-Hessberger furnace.

¹⁰ F. Russ, *Z. Elektrochem.*, 15, 544 (1909); J. Vanderpol, *ibid.*, 17, 431 (1911).

In industrial units two arcs are connected in series electrically, but in parallel as regards the flow of gases. Several furnaces are operated in parallel. The furnaces take about 200 amp. at 5,000 volts, with a power factor of 0.6. The gases leave the furnace at about 1,000° C. (1,832° F.) and contain about 1 per cent of nitric oxide; the yield is about 60 g. (2 oz.) of nitric acid per kw-hr., or 7.3 kw-hr. per metric ton of fixed nitrogen.

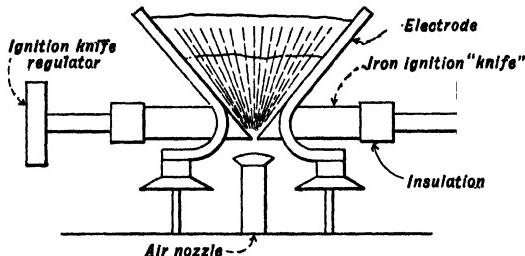


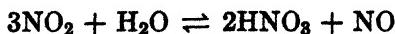
FIG. 238. Pauling arc and electrodes.

Disposition of the Furnace Product. The gases leaving the various types of arc furnaces contain 0.8 to 1.8 per cent nitric oxide at temperatures in the neighborhood of 1,000° C. (1,832° F.). They are conducted to the boiler house where some of the heat is utilized for steam generation. In the boilers the gases are cooled to 200° C. (392° F.). They go from the boilers through iron pipes to the cooling house, where they pass through aluminum pipes cooled on the outside by cold water.

The cooled gases pass to the oxidation chambers, which consist of iron cylinders lined with acid-proof stone, where oxidation takes place according to the reaction



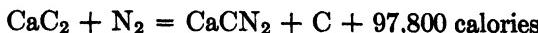
The oxidation proceeds very slowly, and so the velocity of the gases must be very low and the oxidation chambers must be large. The gases then go to granite absorption towers filled with broken quartz. They enter at the base of the first tower, pass up through the quartz packing, then likewise through a number of such towers until the nitric oxide content has been reduced to such a point that an additional tower would not be justified. Water trickles down through the last granite tower and is then piped to the top of the next, and so on through all the towers, and is gradually converted to weak nitric acid:



The solution leaving the towers contains approximately 30 per cent nitric acid.

CALCIUM CYANAMIDE

The cyanamide method of nitrogen fixation is based upon the discovery that, when gaseous nitrogen is passed over calcium carbide at elevated temperatures, calcium cyanamide is formed according to the reaction



The crude cyanamide, also called lime nitrogen, thus obtained is the raw material for the manufacture of fertilizers, ammonia, cyanides, insecticides, and fungicides. The crude cyanamide is a grayish black solid containing about 70 per cent CaCN_2 , 18 per cent free CaO , 12 per cent free carbon as graphite, and small amounts of calcium carbide, iron, aluminum oxides, silica, and other impurities.

Moissan¹¹ found that the rate of nitrification is dependent not only on the temperature but also on the composition of the charge. He found that pure calcium carbide would not react with nitrogen at temperatures up to $1,200^\circ \text{ C.}$ ($2,192^\circ \text{ F.}$). Frank and Caro, however, using commercial calcium carbide, found that nitrogen could be fixed at temperatures considerably below $1,200^\circ \text{ C.}$ But even at temperatures around $1,100^\circ \text{ C.}$ ($2,012^\circ \text{ F.}$) the rate of nitrification was so slow that a large amount of energy had to be supplied to the oven to maintain the charge at the reacting temperature. It was found, however, that certain substances such as alkali and alkali-earth salts acted as catalysts. For example, a carbide containing 10 per cent calcium chloride would take up in 14 hr. at 730° C. ($1,346^\circ \text{ F.}$) as much as 18 per cent nitrogen, the theoretical quantity being 22 per cent, but that carbide alone under similar conditions took up less than 1 per cent nitrogen. The presence of calcium chloride in cyanamide is objectionable, however, for it absorbs moisture and hastens the formation of dicyanodiamide. The use of calcium chloride as a catalyst has been discontinued, and calcium fluoride, CaF_2 , is used in its place. It does not lower the reacting temperature as much as calcium chloride, but 2 per cent of the fluoride is sufficient when intimately mixed with the carbide. It is not objectionable in the finished product.

Raw Materials. The raw materials for calcium cyanamide manufacture are limestone, coal, and air. The limestone and coal are combined to form calcium carbide. The manufacture of carbide was discussed in Chapter XVII, beginning on page 437. The air supplies the necessary nitrogen. No differentiation is made between carbide used for acetylene

¹¹ H. Moissan, *Compt. rend.*, 118, 501 (1894).

manufacture and that used for cyanamide, although it is believed that carbide used for cyanamide does not require as rigid specifications. The carbide pigs are crushed and then ground to 100 mesh, with 85 per cent passing a 200-mesh screen. The grinding is carried out in an atmosphere of nitrogen in order to eliminate the danger of acetylene-air explosion. Before starting, the mills and conveyors are swept out with nitrogen. The catalyst, calcium fluoride, is added in the final grinding mill.

Nitrogen is obtained from the atmosphere by liquefaction and fractional distillation of air. Gas liquefaction has been highly developed, and the cost of nitrogen production forms only about 3 per cent of the total energy consumption including that used for carbide formation. Both the Linde and the Claude processes are suitable. At the U. S. Nitrate Plant No. 2, at Muscle Shoals, Alabama, the liquid-air plant had a capacity of 300 tons of nitrogen per 24 hr. The American Cyanamid Company, in its plant at Niagara Falls, uses the Claude process, in which liquid air is obtained at a pressure of 500 to 600 lb. per sq. in., and a temperature of 229° C. below zero (-380° F.). In the fractional distillation, pure nitrogen gas boils off. Simple distillation of liquid air does not effect a satisfactory separation, but with rectification, nitrogen gas of 99.99 per cent purity comes off at a temperature of -190° C. (-310° F.).

Nitriding Ovens. Two types of nitriding ovens are in use, the continuous and the batch type. The latter are much more common; they were used at the U. S. Plant No. 2 at Muscle Shoals and are used by the American Cyanamid Company at Niagara Falls, Ontario.

More information is available about the ovens at the Muscle Shoals plant than about those at other plants, but from the descriptions available¹² it appears that the ovens in use are constructed somewhat similarly.

The ovens at the Muscle Shoals plant were cylindrical in shape. An outer shell supported on a reinforced-concrete disc is lined with 5 in. of infusorial earth and 5 in. of firebrick. The cover is belled to form a sand seal and is provided with a 5-in. hole in its center for the introduction of a carbon heating pencil or rod.

The finely ground carbide is placed in a cylinder made of heavy paper a few inches smaller in diameter than the oven. A small paper tube surrounds the carbon heating rod. After charging, the double cover is put in place, the carbon rod is inserted, and the current is turned on. Nitrogen piped from the liquid-air plant is admitted to the oven through

¹² The cyanamide plant of the American Cyanamid Company at Niagara Falls, Ontario, is briefly described by J. A. Lee, *Chem. & Met. Eng.*, 38, 564 (1931). References to articles describing the Muscle Shoals plant are found at the end of this section.

the bottom and also through the side near the bottom. The paper tube around the carbon rod is destroyed by the heat, and the carbide surrounding it soon reaches the temperature of nitrification. The furnaces at the Muscle Shoals plant had a capacity of 1,600 lb. carbide; those at the plant of the American Cyanamid Company have a capacity of 8,000 lb. An installation of nitrifying ovens is shown in Fig. 239.



FIG. 239. Nitrifying ovens of 8,000-lb. capacity for preparation of calcium cyanamide. (*Courtesy American Cyanamid Company.*)

The nitriding reaction in the furnace is exothermic, and once started it continues until completed. The period of nitrification from start of the oven to removal of the cold finished product is approximately 1 day per ton of carbide charged.

A continuous nitriding oven has been in use in Sweden for a number of years. It is a tall, vertical, cylindrical structure containing shelves so arranged that the carbide introduced at the top is moved downward from shelf to shelf by means of mechanical scrapers. The nitrogen is admitted at the bottom of the furnace and moves upward. The heat required to start the reaction is furnished by electric arcs at the top of the furnace. The cyanamide is discharged at the bottom. The furnace temperature is stated to be about 950° C. (1,742° F.). About 2 hr. is

required for passage of the carbide through the furnace. The product is obtained as lumps about $\frac{3}{4}$ in. in diameter.

The crude cyanamide contains 61 to 70 per cent cyanamide, 18 to 20 per cent calcium oxide, 12 per cent free carbon, and 1 to 2 per cent unconverted calcium carbide, plus small amounts of miscellaneous impurities introduced by the coke used for the carbide manufacture.



FIG. 240. Cyanamide as it leaves the nitrogen-fixation ovens. (*Courtesy American Cyanamid Company.*)

The carbon is in the form of graphite and gives the cyanamide a slate-gray color.

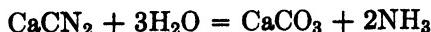
The efficiency of nitrogen utilization is low, perhaps less than half the nitrogen supplied being utilized in the small discontinuous ovens; but since the nitrogen is only a small part of the total cost, this low efficiency is not serious.

Disposition of the Furnace Product. The cyanamide comes from the discontinuous ovens in ingots which must be reduced in size and further prepared in order to be used for fertilizers. Figure 240 shows the cyanamide ingots after removal from the ovens. They are broken up and ground fine in hammer mills. The small amount of carbide remaining in the crude cyanamide is objectionable, for the storage and transportation are attended by considerable risk of acetylene-air explosion unless

the material is packed in air-tight containers. The ground material is therefore treated with enough water to decompose the carbide and to hydrate the lime in the product. An excess of water is avoided because it fosters the formation of dicyanodiamide. About 6 or 7 per cent of water is sufficient to decompose the carbide and hydrate the lime. This amount of water, however, does not reduce the dustiness; therefore the material is treated with 3 to 4 per cent oil by weight of the treated product. A large amount of heat is generated during the hydration process, and since heat and moisture foster the formation of dicyanodiamide, the hydration must be conducted carefully with very thorough agitation of the material while the water and oil are being added. The finished product is cooled by passing through a rotary cooling cylinder and is sent to bulk storage.

Cyanamide is also prepared in granular form. One method is to crush the crude furnace product to the size of rice kernels and then to screen out the fines, but the carbide in the product is objectionable, and its later decomposition and the slaking of the lime, both caused by atmospheric moisture, make the granules crumble gradually to a fine powder. A better method of granulation consists in treating the powdered cyanamide with water either with or without a binding agent and then forming the material into granules under pressure, followed by drying. The greatest bulk of cyanamide manufactured is used directly as a fertilizer or is mixed with other fertilizers.

Ammonia can readily be prepared from cyanamide by treating the material with water and steam under pressure. This process, once used to a considerable extent in supplying a readily usable form of fixed nitrogen, is now obsolete. To obtain ammonia as free from acetylene as possible the finely ground cyanamide is treated with about 2 per cent of water by weight to decompose the carbide. It is then autoclaved with a 3 per cent sodium hydroxide solution first at 60 lb. pressure and later at 120 lb. per sq. in. The reaction can be represented by



The reaction is exothermic and must be controlled by discharge of steam and ammonia from the autoclave. The yield of ammonia on a commercial scale is nearly quantitative. The ammonia can be further oxidized to nitric acid.

Cyanides are produced from cyanamide ¹³ by fusing in an arc furnace a mixture of cyanamide, carbon, usually as a carbide, and common salt. The reaction can be represented by the equation:



¹³ W. S. Landis, *Chem. & Met. Eng.*, **22**, 265 (1920).

The reaction is favored by high temperature so that cyanide is formed largely in the arc zone, but the reaction is reversed at lower temperatures so that rapid cooling is necessary. The carbide is used instead of carbon because it prevents loss of nitrogen during heating.

The furnace is crucible-shaped, tapering toward the bottom. A 12-in. graphite electrode is suspended vertically with its lower end about 12 in. above the bottom of the furnace. The arc forms between the electrode and the hearth, and the charge is fed into the open top of the furnace. At the high current density employed, the charge melts rapidly; it is tapped about every hour. The molten mass tapped at a temperature of about 1,300° C. (2,372° F.), or a little above, is run into a cooling sump where it is stirred with a water-cooled stirrer in the shape of a wheel. In a few seconds the mass is cooled to a black heat and the material is removed by a scraper in the form of thin flakes.

A 90 to 94 per cent conversion of cyanamide to cyanide takes place, and the grayish black product contains 36 to 37 per cent of sodium cyanide. It is used in the metallurgical extraction of gold and for the making of hydrocyanic acid, HCN, for fumigation purposes.¹⁴

¹⁴ More detailed discussion on atmospheric nitrogen fixation will be found in: H. A. Curtis, Ed., *Fixed Nitrogen*, The Chemical Catalog Company, New York, 1932; F. A. Ernst, *Fixation of Atmospheric Nitrogen*, D. Van Nostrand Company, New York, 1928; B. Waeser, *The Atmospheric Nitrogen Industry*, P. Blakiston's Son and Company, Philadelphia, 1926.

CHAPTER XXI

SEPARATION BY ELECTRICAL MEANS

Electrical energy is used in a variety of ways for separating two or more materials from each other. Sometimes worthless or deleterious material is removed from a product, as in the magnetic removal of tramp iron before coal or ore passes into a grinder, or in the removal of water from peat; sometimes a more valuable product is removed from a worthless gangue, as in some types of ore concentration. In other processes the separation is accompanied by a recombination, where the latter phase is the primary object, as in removing rubber from latex and depositing it on cloth or other material.

Other types of separation by electrical means have already been discussed, notably in electrorefining of metals in which a metal in solution is separated from a number of impurities and is deposited in a relatively pure form.

MAGNETIC SEPARATION

It is not the province of this section to discuss the theory of magnetism or the problems involved in the construction of practical and efficient electromagnets. However, a few fundamental statements will aid in clarifying some of the phenomena involved.¹

A coil of wire becomes magnetic when an electric current is passed through it; magnetic lines of force pass around the coil and in more concentrated form through the opening in the coil. Such a coil is called a solenoid. If an iron core is placed through the opening, the lines of force are increased in number and are much more concentrated in the core than they were in the same space without the core. The ratio of the magnetic flux in the iron core to the magnetic field within the solenoid without the core, both with the same current flowing through the coils, is called the permeability of the core material.

The strength of a magnetic field at any point near an electric wire varies directly as the current and inversely as the distance of the point

¹ The physical laws governing magnetic forces on particles are discussed briefly by S. G. Frantz, *Chem. & Met. Eng.*, 45, 274 (1938).

from the wire. This fact introduces two factors that must be balanced against each other in the construction of electromagnets: in order to place *all* the coils of wire as near the core as possible, the wires should be of very small diameter and the insulation should be thin; but to obtain high magnetic flux the electric current through these wires should be large. Obviously the two conditions are incompatible.

The ampere-turn is the magnetomotive force produced by a current of 1 amp. in 1 turn of wire. The total magnetomotive force is directly proportional to the ampere-turns. The unit of magnetomotive force, called a gilbert, is equal to 1.257 ampere-turns.

Residual or permanent magnetism is the flux that remains in the core after the magnetizing current has dropped to zero.

Magnetic Pulleys. A magnetic pulley is placed as the head pulley of a belt conveyor, and remains steadily magnetized by direct current during operation. Non-magnetic materials such as coal or grain drop down directly, owing to gravitational force; but magnetic material, such as iron, is held to the conveyor below the pulley until it is taken so far from the magnetic field that gravitational force is greater than the magnetic force, and the iron drops as shown in Fig. 241.

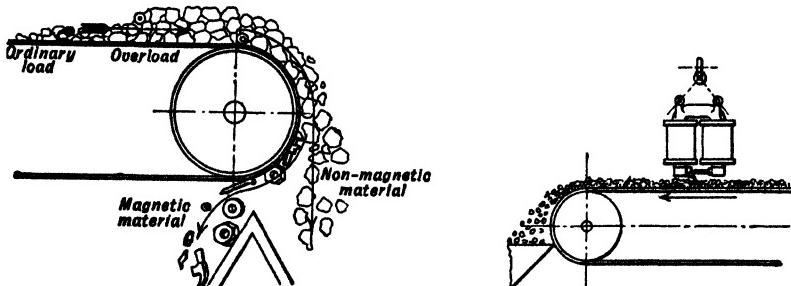


FIG. 241. Separating with a magnetic pulley.

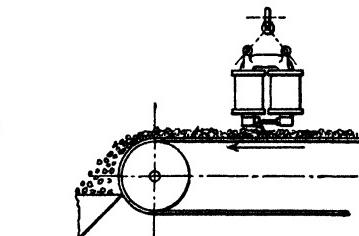


FIG. 242. Separating magnetic from non-magnetic materials with a two-pole electromagnet.

Another method sometimes used is to place the magnetic pulley with a belt above the conveyor pulley, so that the magnetic pulley lifts the magnetic material out of the load of the main conveyor and carries it away on the belt.

Sometimes a portable electromagnet is suspended above a conveyor belt and lifts the magnetic material from the load as shown in Fig. 242.

Magnetic pulleys are machined with crown faces and are made to the dimensions of ordinary head pulleys for belt conveyors so that their installation in a commercial conveyor is relatively simple and inexpensive. Stock sizes of pulleys vary from 12-in. diameter for a 12-in. belt

to 36-in. diameter for a 60-in. belt. The small size has a capacity of 735 cu. ft. per hr. and consumes 390 watts; the large size has a capacity of 23,900 cu. ft. per hr. and consumes 6,534 watts. The capacities given are for installations for removing tramp iron from various materials to protect crushers. Figure 243 is a sectional view of one type of magnetic pulley.

In addition to removing iron from materials to protect crushers and grinders, magnetic pulleys are used for separating iron and steel from foundry sand and foundry refuse and for separating magnetic materials from green garbage and from grain and various seeds.

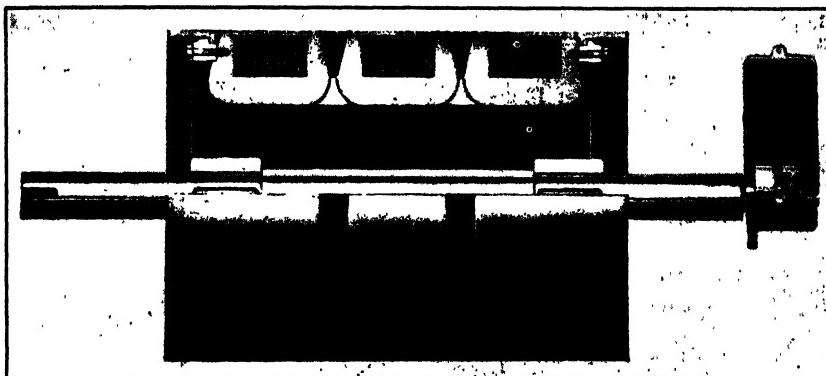


FIG. 243. Sectional view of a magnetic pulley. (*Courtesy Magnetic Manufacturing Company.*)

Disc-Type Magnetic Separator. The disc type of separator is shown in Fig. 244. The material to be treated is placed in a hopper from which it passes onto an inclined vibrating shaker conveyor and is thus fed under a magnet. The magnet itself is a powerful bipolar stationary electromagnet. The poles of the magnet conform to the shape of the outer edge of a rotating disc. This disc is of such a diameter that it extends well over the sides of the vibrating shaker below it. The magnetic lines of force pass diametrically through the disc in a direction parallel to the line of flow of the material to be treated passing under it. The rotating disc is therefore magnetic at its outer edge above the vibrating shaker but not where the rim projects beyond the edges of the shaker. In the Dings type "M" separator a series of secondary induced magnets mounted on the disc become magnetized as they pass under the poles of the large magnet but lose their magnetism as the disc rotates from under the magnet poles. In the type "H" separator of the Magnetic Manufacturing Company, a rotating magnetic yoke with a metal apron around its outer rim constitutes the separating and conveying element.

Any magnetic material, as it passes under the upper pole of the magnet, is picked up by the rotating member and is held until it is carried beyond the inclined conveyor, when it is dropped. Non-magnetic material continues on its course along the conveyor undisturbed. Any magnetic material escaping the upper pole may be caught and removed under the lower pole.

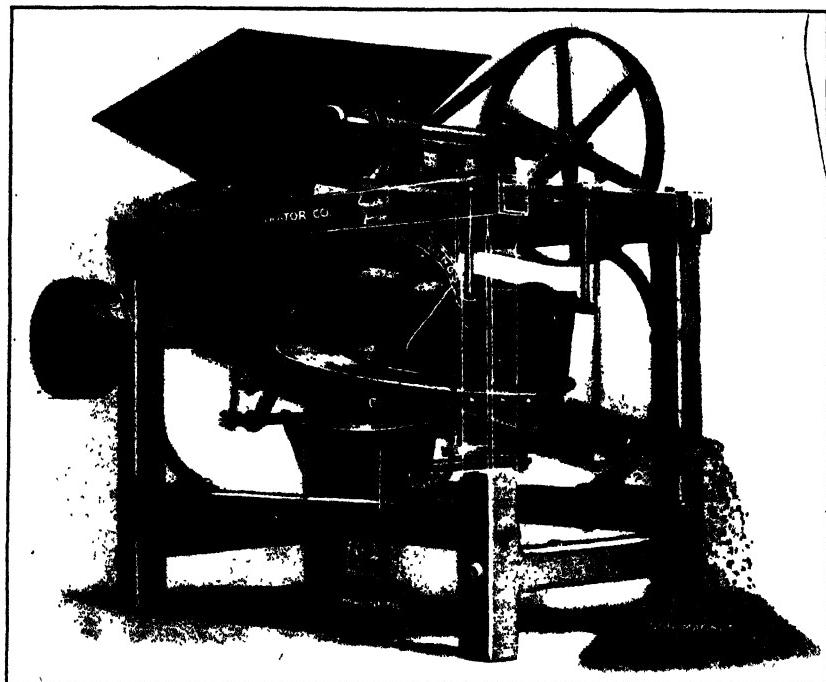


FIG. 244. Disc type of magnetic separator. (*Courtesy Dings Magnetic Separator Company.*)

Disc-type separators are built in capacities of 300 to 1,500 lb. per hr.; they consume from 200 to 660 watts, direct current, for the magnets.

This type of separator is used in foundries, shops, and smelting and refining plants for removing iron from brass, aluminum, and other non-ferrous borings and turnings. It is used for removing iron from glass sand, mineral concentrates of various kinds, rubber buffings, chemicals, grain, cattle and poultry food, and other materials where a fairly clean separation of iron is required.

Wetherill Magnetic Separator. The Wetherill magnetic separator, invented by Wetherill and developed by Payne and Rowand, is designed to produce a more concentrated magnetic field than is obtained with the

other types of separators heretofore discussed and therefore make possible the removal of feebly magnetic materials. It is also possible in the Wetherill separator to separate, from one another, materials with different degrees of magnetic susceptibility.

The operating principle of the Wetherill separator is shown in Fig. 245. The material to be treated must be dry. It flows from the hopper onto the feed roller which spreads it in a thin uniform layer over the

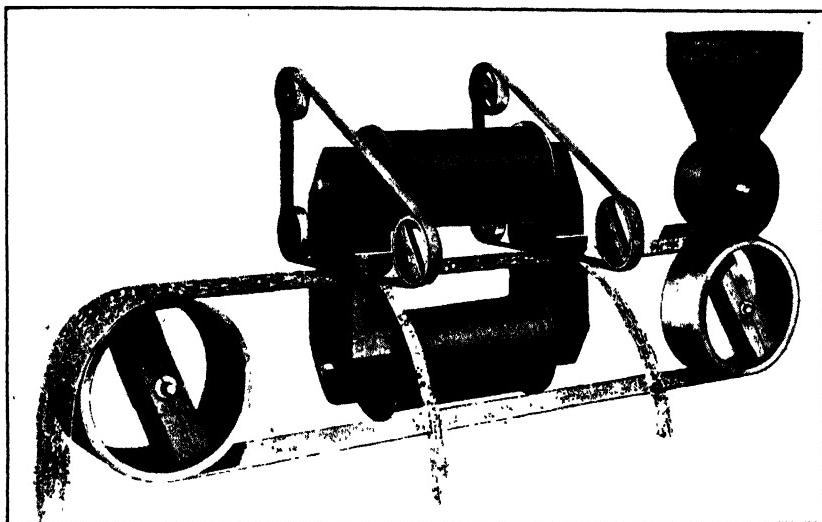


FIG. 245. Diagrammatic illustration of a Rowand-Wetherill high-intensity magnetic separator. (*Courtesy Dings Magnetic Separator Company.*)

whole width of the conveyor belt as it travels toward the poles of the magnets. As shown in the diagram, the poles consist of two horseshoe electromagnets, placed one above the conveyor and one below. The poles of the upper magnet are forged in the form of sharp wedges; the lower ones have flat faces. It is the high magnetic concentration on the upper poles, caused by the converging field, that enables the Wetherill separator to treat materials of low magnetic susceptibility. That is, the magnetic force of the upper wedge-shaped pole exceeds that of the lower, so that, as the conveyor belt with its load passes between the first poles of the magnet, the magnetic particles are strongly attracted by the upper pole and jump towards it. They are intercepted, however, and prevented from reaching the upper pole by a cross-belt which removes them quickly from the magnetic field and allows them to drop at one side. The Rowand-Wetherill separator is constructed with one, two, or three double magnets giving two, four, or six poles, each double

magnet having a rheostat for regulation of the current strength. For instance, in one size of separator the first magnet has 30,000 ampere-turns, the second 60,000, and the third 100,000. In the treatment of monazite sand, magnetite is removed by the first magnet, ilmenite by the second, leaving the monazite to be lifted from the worthless sand by the third and most powerful magnet.

The capacities of Wetherill separators depend upon the nature of the material treated and the degree or type of separation required; they range from 0.25 to 15 tons per hour, and consume from 4 to 60 amp. direct current at 110 volts.

The Wetherill separator has found considerable application in the metallurgical industries. In the zinc industry, marmatite, a ferruginous sphalerite which is slightly magnetic, is separated from raw pyrite by the most powerful Rowand-Wetherill magnets. Non-magnetic zinc-iron-sulphide ores require a light roast to make the pyrite magnetic, and a separation is then accomplished by low-strength magnets. At Franklin Furnace, New Jersey, franklinite, fowlerite, and garnet are separated from willemite, zincite, quartz, mica, and calcite magnetically.

In treating tungsten ore, non-magnetic scheelite travels off the end of the machine while the wolframite is removed by the magnets. Crude Montana manganese ore is concentrated magnetically without any additional apparatus. The Rowand-Wetherill separator is used for the separation of pyrrhotite from other sulphides, garnet, or gangue; of roasted chalcopyrite from iron or nickel sulphides; roasted limonite from smithsonite and calamine; and a variety of other separations.

The development of high-intensity magnetic separators has made their use practicable where other devices have failed. However, they have a number of limitations. If the material is not properly ground or screened, operation is unsatisfactory. The range is about 12 to 80 mesh, and their capacities are greatly reduced or they fail entirely in the handling of dry fines. With some materials separation is incomplete under the most favorable circumstances, and the product comes from the separators badly mixed.

Magnetic Separation from Solutions and Suspensions. Sometimes it is necessary to remove iron from suspensions, such as clay slips for pottery manufacture. Figure 246 shows a Dings magnetic separator as used for clay slips. It consists of a number of electromagnets enclosed in water-tight brass or copper casings. A removable brass tray is placed over the magnets and is fitted with auxiliary magnets located directly over the poles of the enclosed electromagnets.

The liquid flows over the trays through and around the auxiliary magnets, which project above the surface of the liquid. These magnets

are placed in staggered rows so as to insure intimate contact with all portions of the slip. Adjacent rows are of opposite polarity. The separator is cleaned by opening the electric circuit and washing off the accumulation of iron and iron oxides.

The discharge from the separator passes over a collapsible spout which is held in position by a magnetic latch. If the magnetizing current fails,

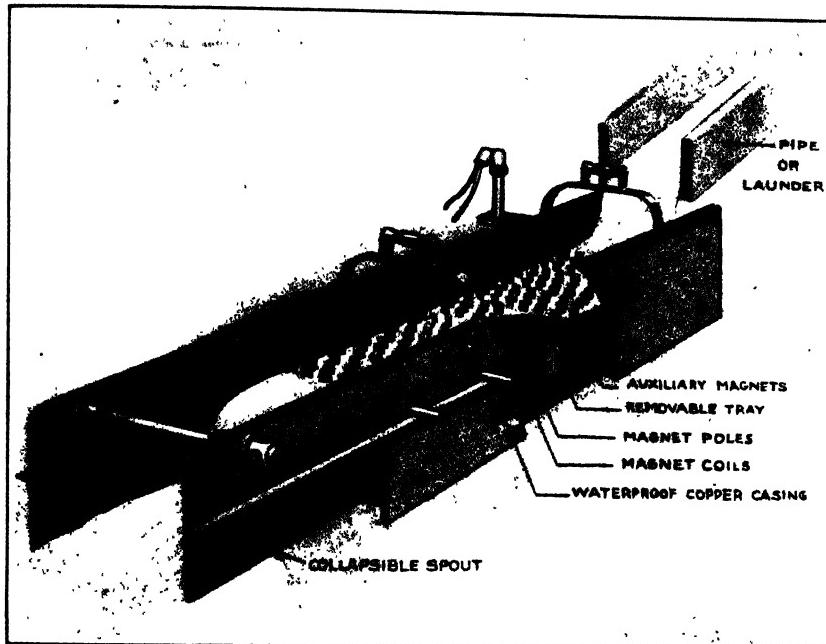


FIG. 246. Dings magnetic separator for pottery clay slips. (*Courtesy Dings Magnetic Separator Company.*)

the spout is released and it drops to divert the slip to a separate storage tank, thus preventing the accumulated iron from releasing and passing on into the cleaned slip. The separator requires no mechanical drive and has no moving parts.

The separators are built in sizes ranging from 400 to 1,600 gal. per hr. and consume 175 to 700 watts, direct current, at 110 volts.

Another magnetic separator for liquids, but of a different type of construction, is the Stearns, shown in Fig. 247. The clay slip enters the funnel-shaped copper tray at the top and is made to pass through the magnetic gap in a thin stream. The thickness of the stream flowing over the cone can be adjusted by rotating the copper tray; for the average pottery slip the thickness of the stream is about $\frac{1}{8}$ in. Consequently, the material passing through the magnetic field permits iron

specks to contact directly with the strong fields of the magnet where they are retained. As a protective device against contaminating cleaned slip in case of power failure, the slip, as it leaves the separator, passes through a valve which is held open by a solenoid. The solenoid is connected electrically in series with the magnet, so that the valve closes if the magnetizing current is interrupted.

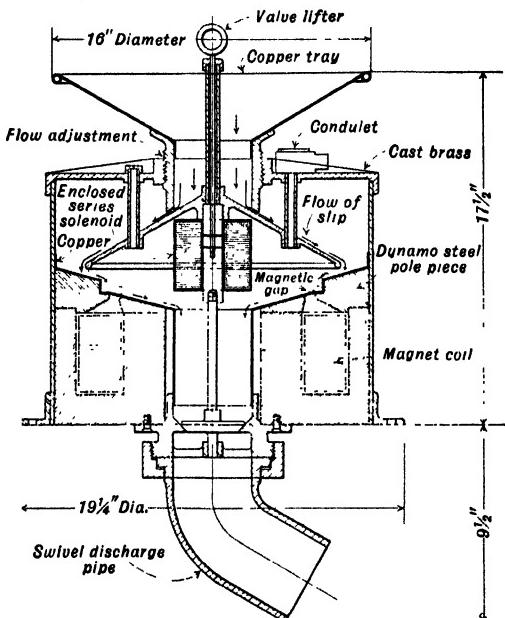


FIG. 247. Stearns magnetic separator for fluids. (*Courtesy Magnetic Separator Company.*)

At the close of the day's work the accumulated iron can be flushed out, with the current cut off, the valve being held open by means of the valve lifter ring at the top.

The capacity of the Stearns separator is approximately 1,200 gal. per hr. The energy consumption is 275 watts, direct current, at 110 volts.

The widest application of the wet-type separator is found in the ceramic industry where all body and glaze slips used for whiteware manufacture must pass through or over magnets to remove any contained iron. Fine specks of iron or iron oxide in the body will show up as pronounced ugly spots in the fired ware. It is also used for removing iron from ink introduced during the grinding process, and for removing iron from finely ground barytes. Unlike the dry magnetic separators, the wet separator operates best on finely ground materials.

Induction Magnetic Separator. In most types of magnetic separators thus far discussed the separation depends upon the magnetic force acting in a vertical plane in direct opposition to the force of gravity. The induction magnetic separator is based on the fact that a particle

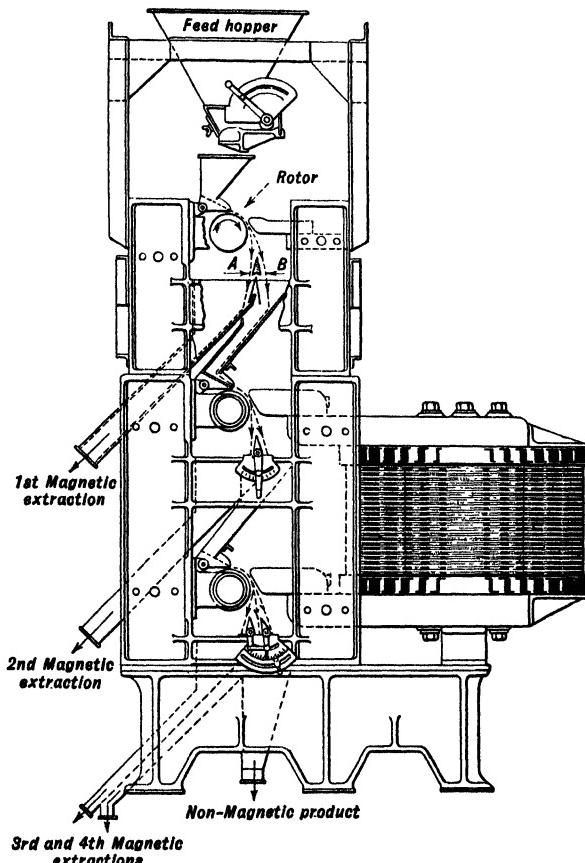


FIG. 248. Johnson induction separator.

falling freely in air may be more readily *diverted* from its path of flight than *lifted* in opposition to the force of gravity. Advantage can be taken, therefore, of very slight differences in magnetic susceptibilities, and this principle has made possible separations which could not be accomplished by separators of other types. This type of separator is finding extensive application.

Two styles of separators are shown in Figs. 248 and 249, respectively. The induction machine consists of a large primary electromagnet of the

horseshoe type, which is the most efficient design. The pole pieces are tapered and interposed between these poles, and the bridge bar or keeper are laminated rolls, one opposite each pole. The keeper, forming the bridge bar between the two poles, has its end shaped to conform to the curvature of the rolls. There is a minimum clearance between the keeper and the rolls to reduce flux resistance, so that in reality there is only one air gap at each pole.

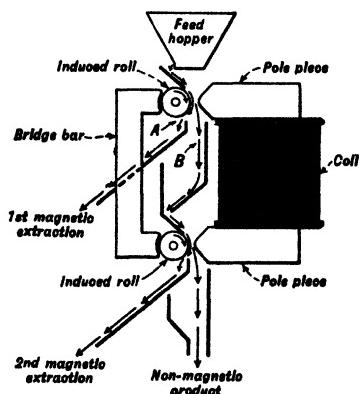
The material to be separated is fed in grain or granular form from a hopper to the series of rolls or rotors, each highly magnetized and revolving in a magnetic field. The revolving action of the rotors tends to throw

the grain by centrifugal force, and the grain in falling assumes a trajectory or arc. Grains of magnetic material are attracted to the rotor and retained on it for a longer period of time than grains of non-magnetic materials. Hence, grains of non-magnetic materials assume a normal trajectory or arc, *B*, Fig. 248, while grains which have been attracted to the rotor resist centrifugal force and assume a different arc *A*. An adjustable knife-edge divider directs the flow of grain stream and discharges magnetic extractions from the machine. A magnetic as well as a non-magnetic or less-magnetic product is produced

FIG. 249. Dings induction separator.

by the first or top rotor; but the magnetic portion, consisting of bits of magnetic and non-magnetic particles attached to each other, is again passed through the magnetic zone immediately below where particles that have not been extracted in the first field are taken out. The second rotor has a greater magnetic intensity because of the smaller air gap between it and the pole piece. For some materials it is necessary to have four and even six rotors, each successive rotor being of greater intensity than the one preceding it.

Classification of material according to size before treatment is an important factor. The fines of some substances have a tendency to stick to the surface with which they come in contact, and obviously they must, therefore, be eliminated before separation. But even though the fines do not show this tendency to adhere to surfaces and it is attempted to separate all sizes, from the finest to the coarsest, inertia of the large sizes and lack of inertia of the small sizes clearly offset the relative attraction of the magnet for them.



If fine iron or other strongly magnetic particles are present the machine is provided with a relatively low-intensity scalping rotor directly below the feeding hopper as shown in Fig. 248. It separates these strongly magnetic particles and prevents fouling of the heavily induced lower rolls.

Induction magnetic separators are finding application for separation of materials of such low magnetic susceptibility that they had been considered entirely non-magnetic and therefore not amenable to magnetic separation. The separator was first developed for use in the abrasive industry, and its success has extended its field of usefulness to other ceramic materials. Table XXXIII gives a list of minerals with

TABLE XXXIII
RELATIVE MAGNETIC SUSCEPTIBILITIES OF VARIOUS MINERALS

Iron = 100

Apatite	0.21	Ilmenite	24.70
Argentite	0.27	Leucite	34.62
Arsenopyrite	0.15	Limonite	0.84
Biotite	3.21	Magnesite	0.15
Bornite	0.22	Magnetite	40.18
Calamine	0.51	Manganite	0.52
Calcite	0.03	Molybdenite	0.23
Celestite	0.10	Niccolite	0.04
Cerargyrite	0.28	Orthoclase	0.05
Cerussite	0.30	Pyrite	0.23
Chalcocite	0.09	Pyrolusite	0.71
Chalcopyrite	0.14	Pyrrhotite	6.69
Cirabar	0.10	Quartz	0.37
Corundum	0.83	Rutile	0.37
Cryolite	0.05	Senarmontite	0.05
Cuprite	0.08	Siderite	1.82
Dolomite	0.22	Smithsonite	0.07
Enargite	0.05	Sphalerite	0.23
Fluorite	0.11	Stibnite	0.05
Franklinite	35.38	Talc	0.15
Galena	0.04	Tetrahedrite	0.21
Garnet	0.40	Willemite	0.21
Gypsum	0.12	Witherite	0.02
Hematite	1.32	Zincite	0.10
Iron	100.00	Zircon	1.01

their relative magnetic susceptibilities, that of iron being arbitrarily taken as 100. The table, however, is only an approximation, presented chiefly to show the wide variations encountered. Minerals vary widely in their composition and therefore in their magnetic susceptibilities.

For instance, the relative susceptibility of garnet is given as 0.40, but some garnets may have a value more than ten times as great.

The induction separator is being used for separating muscovite mica from feldspar, for producing a cyanite and silicate concentrate of extremely low iron content, for extracting ilmenite from garnet and quartz, and experimentally it is being used for separation of ash from anthracite coal.² It has found many other successful applications and no doubt will find many more.

ELECTROSTATIC SEPARATION

Huff Electrostatic Separator. Electrostatic separation is the result of the work of Blake and Morscher. The principle of the early Blake-Morscher separator is shown in Fig. 250a. Good conductors on making contact with the charged rod take on a like charge and are repelled; poor conductors require a longer time to become charged and, therefore, in the short time they are in the electrical field are unaffected and fall downward. The Blake-Morscher machine is impracticable and has been largely superseded by the Huff separator.

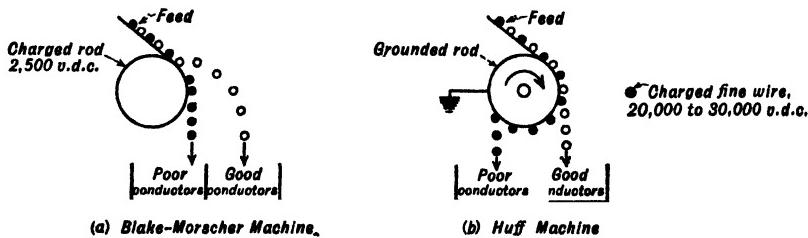


FIG. 250. Two types of electrostatic separators.

The Huff electrostatic separator is shown diagrammatically in Fig. 250b. A highly charged fine wire is placed parallel to a grounded metallic rod or roll, which, in the type shown, rotates. Conducting particles receive a charge in the electrostatic field between the charged wire and the grounded roll, but they transmit their charge immediately to the roll and ground and are therefore unaffected and fall normally. Poor conductors become charged on the face toward the wire, which charge induces a charge of opposite sign on the adjacent face of the roll. The particles therefore cling to the roll until their charges dissipate by conduction or until the clinging particles are removed mechanically.

Static electricity is provided by a 4-hp. motor-generator set, the generator being rated at 300 volts and 5 amp. The alternating-current

² G. W. Jarman, Jr., *Bull. Am. Ceram. Soc.*, 18, 126 (1934).

voltage is stepped up in a transformer to between 20,000 and 30,000 volts. A mechanical rectifier, mounted on the end of the motor-generator shaft, converts the current to a unidirectional current.

The Huff separator is used for separating pyrite from blende if little or no pyrite is occluded, and for removing iron-containing grains from silicon carbide, fused alumina, and feldspar. The machine will not

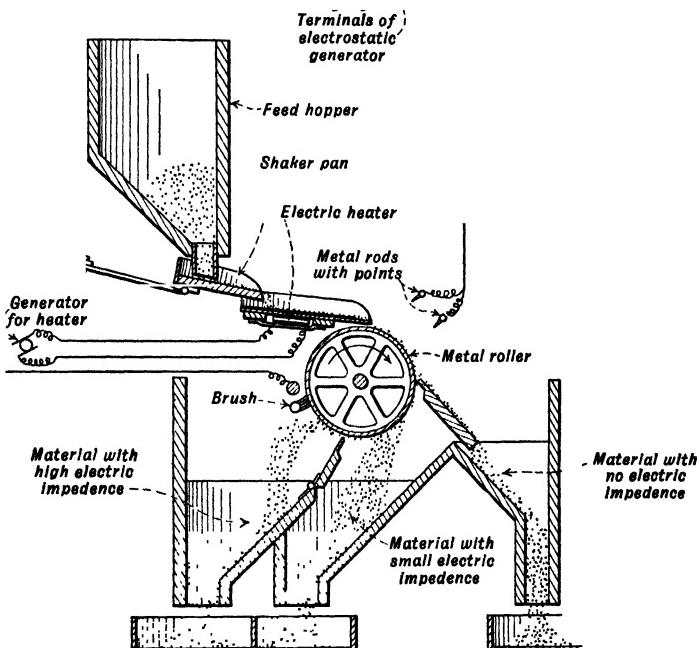


FIG. 251. Sutton, Steele, and Steele electrostatic separator.

handle very fine dust, and for fairly clean separation the grains should be screened to nearly uniform size. A number of Huff separators are in use in the metallurgical and abrasive industries, but it is no longer being manufactured as a commercial item.

Sutton, Steele, and Steele Electrostatic Separator. The Sutton, Steele, and Steele electrostatic separator,³ shown diagrammatically in Fig. 251, depends upon the difference in either the electrical conductance or the specific inductivity of the particles to be separated. The grain to be treated should be dry, and as the feed leaves the hopper it passes over a table that can be heated electrically. As the particles pass into

³ H. M. Sutton, W. L. Steele, and E. G. Steele, Apparatus for separating substances of different dielectric capacities, U. S. Patent 1,386,287, Aug. 2, 1921. H. M. Sutton and G. W. Jarman, Jr., *Chem. & Met. Eng.*, 45, 277 (1938).

the electrical field the non-conductors receive a bath or spray of electricity from one or more rows of points, only one point in each of two rows being shown in the illustration. The particles, while in contact with a revolving electrode or roller, have charges built up on the side opposite to the roller to which they come in contact. This roller is connected to the opposite pole of the electrostatic generator. Fine particles adhere with such tenacity that a brush may be necessary on the opposite side of the electrode to remove them. Conducting particles, on the other hand, fall inert from the electrode. This type of machine is used for separating mica from graphite, copper pyrites from zinc blende, barium from zinc blende, and for similar separations.

Cottrell Electrostatic Precipitator. The removal of suspended particles from gases was first suggested in 1824 by Hohlfeld, a teacher at Leipzig, Germany. He observed that, if he electrified a wire hung in a bottle filled with smoke, the smoke cleared rapidly and a deposit formed on the inside of the bottle. In 1884 Sir Oliver Lodge in England rediscovered the phenomenon, and in 1885 a commercially unsuccessful attempt was made to utilize this effect in a lead plant in Wales.

The present-day successful commercial application of the process of electrostatic precipitation of dust and fume is due to the work of Dr. F. G. Cottrell, who started the necessary experimental work in 1906, and the precipitators developed are widely known as Cottrell precipitators, or simply as "Cottreells" in industrial parlance.

If an electrically charged particle is in an electrical field between two electrodes it will tend to move toward the negative pole if charged positively and toward the positive pole if charged negatively. The suspended particles may receive charges from ionized gases, or their charges may be induced if they pass through an electrical field. The mechanism of ionization of a gas into positive and negative ions was discussed in Chapter XVIII, page 471. The ions and electrons in an ionized gas may remain free or become attached to suspended particles such as dust, soot, or vapor droplets. These charged agglomerates tend to move across the electric field to the electrode of opposite charge.

Charged particles in an electric field tend to migrate toward the weakest part of the field. If, for instance, one electrode consists of a metal pipe and the other of a wire suspended axially in the pipe, and a potential is applied to these two electrodes, the field around the wire will be intense but its intensity will gradually diminish radially toward the pipe. The molecules of the gases which have become ionized and the suspended particles to which electric charges are attached are propelled rapidly through the gases by the force of the electric field, the direction being mainly from the strongest to the weakest part of the field, i.e., from

the wire to the pipe surrounding it. The movement of these particles and molecules has an aspirating effect upon adjacent gas molecules, setting them in motion, producing what is commonly called "electric wind." It is true that charges of both positive and negative signs are present in the gases and that they tend to move in opposite directions, but those which tend to move countercurrent to the electric wind have to overcome considerable resistance and are probably swept back or neutralized, especially if these charged particles are carrying suspended par-

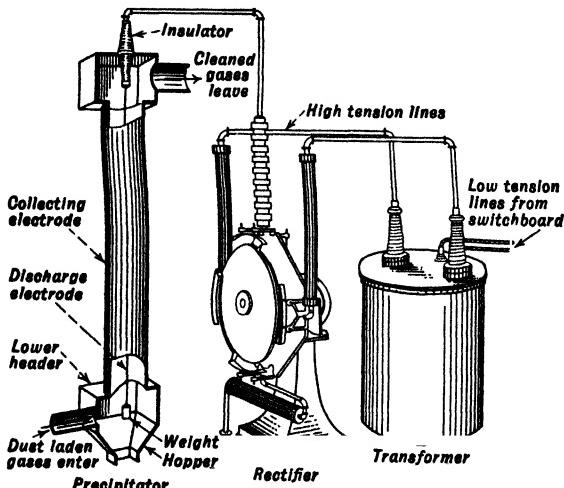


FIG. 252. Cottrell electrostatic precipitator. (Courtesy Western Precipitation Company.)

ticles with them. The net result is that practically all the suspended particles are deposited on the pipe, which is called the collecting electrode.

It would appear from the above discussion that it is immaterial what the polarity of the electrodes is, provided that they are opposite, for in either event the electric wind moves from the field of high intensity to the lower intensity, i.e., from the central electrode to the outside collecting electrode. But by making the central electrode of negative polarity, the movement of the gases is produced by electrons and negative ions, which have a higher velocity than the positive ions, and the results described above are then the most pronounced and satisfactory.⁴

A typical set-up of a commercial precipitator is shown in Fig. 252. Gases to be treated enter the precipitator through the lower header and pass upward through the pipe wherein they are subjected to the high

⁴ The theory of electrostatic precipitation is treated more fully by F. G. Cottrell, *Smithsonian Inst. Rept.*, 1913, p. 653, Pub. 1307; and W. W. Strong, *Proc. Am. Inst. Elec. Engrs.*, 34, 397 (1915).

electrical potential maintained between the discharge electrode and the inside of the pipe which serves as the collecting electrode. Voltages of 20,000 to 100,000 volts direct current are used. The suspended particles become charged and deposit on the inside of the pipe, while the cleaned gases pass on to the upper header and out of the precipitator through a suitable flue.

If the material deposited on the collecting electrode is a liquid it flows down the surface to the hopper, but if the nature of the material is such that it does not flow, as when powdered materials are collected, it is dislodged by a rapping device on the pipe and falls into the hopper of its own weight. The precipitated material is removed from the hoppers by means of screw conveyors or other devices.

Collecting electrodes may be in the form of pipes, plates, screens, curtains of rods, or wire; the discharge electrodes are usually wires or rods. The direction of the gas flow may be vertical or horizontal; in the vertical-flow precipitator, up or down draft may be employed.

Precipitators are usually built of steel, but if corrosive gases are treated, lead or other corrosion-resistant materials are used. In many installations, particularly in the collection of dust and fume from cement kilns, or other dry gases, the collecting electrodes may be of special graded resistance type, being so constructed as to offer a graded resistance to the electrical current to insure a better distribution of the electrical field.

The precipitator operates over a wide range of temperature; it treats, with equal facility, gases at 30° C. (86° F.) or 800° C. (1,472° F.). It is necessary, however, in a few instances to humidify the gases or to add electrically conducting materials in order to secure proper conductivity of the deposited dust and fume, for otherwise it may be impossible to maintain the necessary voltage for proper precipitation.

It is necessary, for the proper operation of an electrical precipitator, to obtain a unidirectional current of high voltage, namely 20,000 to 100,000 volts. The voltage is stepped up in a transformer and is then rectified either by a mechanical rectifier or by a Kenotron. Figure 253 shows a mechanical rectifier which consists of four conducting points mounted 90° apart on a non-conducting plate attached to the shaft of a synchronous motor. Each point is connected electrically to another adjacent point along the circumference of the disc.

The rectified current may also be obtained by means of a Kenotron. A Kenotron is a thermionic rectifier manufactured by the General Electric Company, the principle of which was discussed in Chapter XVIII beginning on page 476. A single Kenotron will rectify only one-half of the applied alternating current wave, but with a combination of

four Kenotrons it is possible to rectify both waves and to utilize the full maximum value of the alternating-current voltage. A unit of four KC-1 Kenotrons has a capacity of 500 ma. direct current, at a maximum voltage of 100,000, corresponding to an effective value of about 71,000 volts alternating current. That is, four Kenotrons will rectify about 30 kw.

Electrical precipitation has found wide industrial application. A precipitator serves one of two useful purposes: the removal of valuable

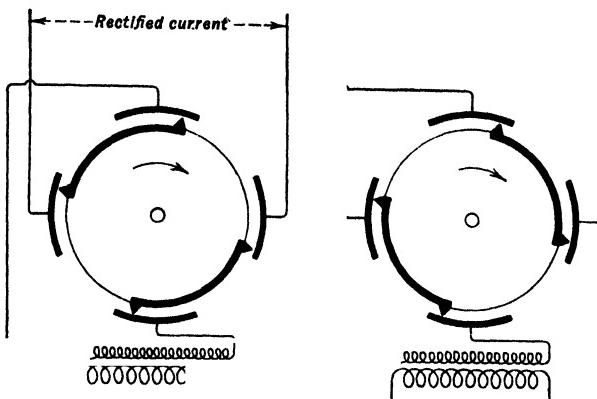


FIG. 253. A mechanical rectifier.

dust or fume from a gas, or the removal of harmful or objectionable suspensions from a gas; frequently both ends are achieved at the same time. A complete discussion of the various applications would require more space than can be allowed here. However, some of the chief applications are briefly enumerated.

Substantially all present-day non-ferrous reduction works employ electrical precipitation to recover furnace losses. Lead, copper, and zinc reduction works operate mainly on sulphide-bearing ores, so that a roasting process is necessary. Roasting of present-day flotation concentrates is productive of extremely heavy furnace losses through dust and fine ore particles carried from the furnace with the exit gases. Such losses commonly exceed 5 per cent and with hard driving of the furnaces may reach 10 per cent of the charge. At a large smelter where gases are treated from multiple-hearth furnace roasters operating on copper ore and flotation concentrates, 7 tons of dust is collected per roaster daily, the collecting efficiency averaging 97 per cent.⁵ Some reduction fur-

⁵ The collecting efficiency refers solely to the percentage of suspensions removed.

naces have sufficient losses to justify the installation of precipitators. In one lead smelter the daily collection from four blast furnaces is 40 tons of dust, averaging 60 per cent lead. Subsidiary and associated metals occurring with lead and copper, such as zinc, gold, and silver, may be recovered from the furnace gases by electrical precipitation.

In a cement mill equipped with 125-ft. kilns, 18 tons of dust is collected per day per kiln at an efficiency of 98 per cent. The cement dust is especially rich in potash. Not only is the dust collected of value, but if not removed from the stack gases it has a deleterious effect on the health of the community.

In sulphuric acid manufacture, dust or other suspended material is carried with the furnace gases when sulphide ores are roasted; the gases are readily cleaned by electrical precipitation before entering the towers in chamber plants or the contact chamber in contact acid plants. In oil refineries where the sulphuric acid from the acid sludges is recovered and concentrated, acid mist allowed to discharge into the atmosphere constitutes a nuisance. Such mist or fog of sulphuric acid is readily removed and collected by electrical precipitation.⁶

Electrical precipitation has come into extended use in connection with the cleaning of combustible gases, particularly the removal of tar fogs from city manufacturered-gas supply systems.

Electrostatic Air Cleaning. The Precipitron. The Precipitron appeared as a commercial article⁷ in 1937. The basic principle is the same as in the Cottrell system, but the Precipitron applies it differently. It is used in ventilating systems where the amount of dust is small as compared to industrial systems and the corroding effects of the gases are usually absent. Therefore ruggedness, large wires, and wide plate spacings are not necessary. The smaller ionizing wire permits greatly reduced voltage and therefore closer plate spacing; the potential required for ionization is directly proportional to diameter of the ionizing wire.

The Precipitron uses a tungsten wire 5 mils in diameter. It requires an ionizing potential of about 12,000 volts; this means smaller, less-expensive equipment, and, even more important, the corona is such that the amount of ozone formed is no more than that produced by sunlight in ordinary air.

The ionizing wire is made positive instead of negative as in the Cottrell precipitator. This entails a slight sacrifice in ionizing efficiency but gains a 10 to 1 reduction in ozone formation. The dust-ionizing and dust-collection functions are separated. In the ionizing section the ionizing wires are held between tubes oppositely charged. A dust particle as it

⁶ O. U. Lawrence, *Chem. & Met. Eng.*, 45, 280 (1938).

⁷ Westinghouse Electric and Manufacturing Company, Cleveland, Ohio.

passes between a wire and a tube is charged positively and is swept into the collector section which consists of parallel plates of opposite charge, 5,000 volts to ground, as shown in Fig. 254. Here the strong field drives the positively charged particle out of its line of flight to the negative plate.

The Precipitron electrostatic air cleaner is made in cell form, each 36 in. high by 8 in. wide, including an ionizing and a collecting chamber. Each cell has a rating of 600 cu. ft. of air per min. for 90 per cent cleaning efficiency. Cells are stacked one on top of another and side by side as required to accommodate the amount of air circulated.

Energy is supplied by a power pack, which comprises a high-voltage transformer, vacuum-tube rectifier, and capacitors to smooth out the pulsating direct-current voltage. The total energy consumption is about 110 watts for twelve 36-in. cells. The power factor is 75 to 80 per cent.

The Precipitron is used for cleaning air for office buildings, stores, auditoriums, libraries, hotels, and restaurants, as well as in manufacturing establishments where clean air is necessary, as parts of aircraft-engine factories or where optical-glass is ground and lens assemblies made or where photographic emulsions are prepared. Although the Precipitron is chiefly installed in commercial establishments, the potential demand for use in home forced-air heating and cooling systems is probably very large. A representative unit for a medium-sized home has a power input of 80 watts.

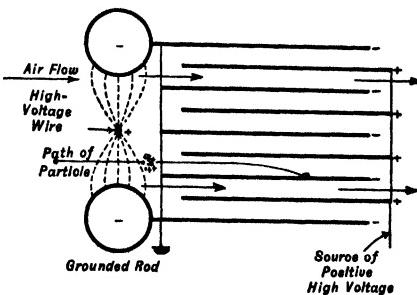


FIG. 254. Schematic diagram of the Precipitron for electrostatic air cleaning. (Courtesy Westinghouse Electric and Manufacturing Company.)

ELECTROKINETICS: COLLOID ELECTROCHEMISTRY

A characteristic feature of colloidal systems is the existence of positive or negative charges on the colloidal particles. The presence of these charges is shown by the fact that when colloidal particles are placed in an electrostatic field they migrate to the negative or to the positive pole. This phenomenon, the migration of colloidal particles in an electrical field, is called electrophoresis or cataphoresis. Many more colloids carry negative charges than positive charges. Table XXXIV lists some typical colloids classified according to their charges in

aqueous solution. The nature of the charge may vary with the dispersion medium used. Some colloidal solutions in turpentine, for example, have charges opposite to those in water.

TABLE XXXIV
ELECTRICAL CHARGES OF HYDROSOLS

Electropositive:		Electronegative:	
Particles migrate to cathode		Particles migrate to anode	
Bismarck brown	Aniline blue	Metallic sulphide	
Hemoglobin	Clay	Rubber latex	
Magdala red	Cotton	Shellac	
Metallic hydroxides	Eosine	Silk	
Methyl violet	Graphite	Starch	
Methylene blue	Indigo	Sulphur	
Titanic acid	Metals		

If a porous diaphragm divides a glass cell into two parts and both halves are filled with a feebly conducting liquid, with an electrode dipping into each part of the cell, it will be found that on passage of a current the liquid will begin to rise on one side of the diaphragm and will continue to do so until a definite equilibrium is established. The majority of substances acquire a negative charge when immersed in water, so that water, under these conditions, becomes positively charged and will migrate to the cathode. Certain substances, however, acquire a positive charge when immersed in water, and under such conditions the water will migrate to the anode. This phenomenon, the migration of water through a porous diaphragm in an electrical field, is called electroendosmosis.

Cataphoresis and electro-osmosis may be looked upon as the reverse of each other, although actually they are but different physical manifestations of the same phenomenon: the relative motion of two phases in opposite directions.⁸

These phenomena have found a number of interesting applications even if most of the applications have not received widespread adoption or have not progressed beyond the experimental stage.

Dewatering of Clays. A process for dewatering clay suspension by cataphoresis developed by Count Schwerin⁹ in Germany has been

⁸ A more complete discussion of the fundamental principle involved is given by Creighton in Vol. I, and by works on physical chemistry such as Frederick Gethman and Farrington Daniels, *Outlines of Physical Chemistry*, seventh edition, John Wiley & Sons, New York, 1948.

⁹ M. Stoermer, *Tonind. Ztg.*, 36, 1283 (1912); W. R. Ormondy, *Trans. Ceram. Soc. (England)*, 12, 36 (1912-13).

studied by Bleininger.¹⁰ Clay particles when suspended in water become negatively charged and will migrate to the anode. The clay is first blunged and screened, which removes a number of impurities such as sand, feldspar, and pyrites. Bleininger found that the addition of a small amount of electrolyte, such as sodium hydroxide or sodium oxalate, in just the proper amounts to decrease the viscosity of the slip to a minimum, is a very important factor in the process. The sodium phosphates and silicates are reported as being the best for the purpose.¹¹ The amount of reagent used is small, never exceeding 0.2 per cent in terms of the dry weight of the clay. Results obtained with a variety of different operating conditions have received renewed study.¹²

The clay slip is placed in a cell with a revolving metal drum anode and a wire net cathode suspended beneath it. The voltage across the electrodes ranges from 80 to 180 volts.

The only plants using the electrical method in the clay industry are located in Germany and Czechoslovakia. At one plant¹³ the fine clay remaining in suspension after purification by washing is fed to six cataphoresis machines which deliver the material in a continuous sheet $\frac{1}{8}$ in. thick and 5 ft. wide, containing an average of 35 per cent of water. The depleted suspension is pumped back to the head of the plant. The dewatered clay is pressed into tubes and is further dried in tunnel driers. According to reports, the capacity of the plant is 78 tons of clay per 24 hr.

If the temperature of the suspension is allowed to rise above a certain maximum, approximately 40° C. (104° F.), the efficiency of the process is decreased, owing to the increased conductivity.

The cataphoresis process removes clay from water but does not effect any appreciable purification of clay. The electrical process therefore merely competes with the filter press, the choice between the two being a matter of comparative costs. At the present time no exact figures are available for comparison.

Dehydration. Some materials when wet retain the water very tenaciously. No satisfactory method has been found for drying them. Air drying is very slow; drying by heat requires excessive amounts of energy; and pressing removes but small amounts of water. Cataphoresis and electroendosmosis appeared as a possible method for accomplishing such

¹⁰ A. V. Bleininger, *Bur. Standards Tech. Paper* 51 (1915); *Trans. Am. Ceram. Soc.*, 15, 335 (1913).

¹¹ O. C. Ralston and M. Hoseh, *Trans. Electrochem. Soc.*, 80, 85 (1942).

¹² S. Speil, *Bull. Am. Ceram. Soc.*, 20, 244 (1941); S. Speil and M. R. Thompson, *Trans. Electrochem. Soc.*, 81, 119 (1943).

¹³ Anon., *Ceram. Age*, 16, 165 (1930); C. E. Curtis, *Trans. Electrochem. Soc.*, 73, 503 (1938).

dehydration and have been the subject of considerable study, particularly by Schwerin in Germany for the removal of water from muds, pulps, and spongy or jellylike materials. The investigations have centered especially on peat, which occurs in many places as a slimy material containing more than 90 per cent of water.

On account of the sliminess of peat, filtration and centrifuging are not satisfactory because the peat forms an almost impervious layer on the filter or the centrifuge. In drying processes it requires 880 B.t.u. per lb. to reduce the moisture content from 90 to 50 per cent, but, even if the peat is further air-dried to a moisture content of 20 per cent, the calorific value is only 810 B.t.u. per lb.

Count Schwerin¹⁴ found that, if peat is placed between a plate anode and a wire gauze cathode, it is carried to the anode where it is deposited as a crust containing 50 to 60 per cent moisture. The potential gradient is 4 to 5 volts per cm., and 0.37 to 0.42 kw-hr. is required to remove 1 cu. ft. of water. The process, however, has not attained commercial success, for electroendosmosis does not remove sufficient water to make the peat ready for use as a fuel, and subsequent air drying is too slow and costly.

Electrical Lubrication. In the manufacture of bricks and heavy clay structural material out of clay by the stiff mud process the plastic clay is extruded through a die, in the form of a column or bar, which is cut into proper lengths by means of wires to produce bricks or other clay articles desired. The proper lubrication of the die is necessary to prevent the formation of serrated edges and to reduce to a minimum the difference in velocity of the extruded clay between the inside of the column and the outside. Differences in velocity of the clay column on the inside and outside cause a laminar structure which weakens the finished product. Common lubricants are water, steam, oils, and emulsions.

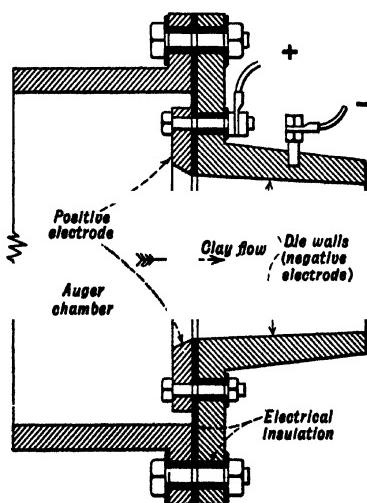


FIG. 255. Simple solid-column die, wired for electrical lubrication.

Under certain conditions electroendosmosis supplies sufficient water at the die surface for lubrication. An insulated anode is placed in the

¹⁴ Count B. Schwerin, *Z. Elektrochem.*, 9, 739 (1903); *Ber. V. int. kong. angew. Chem.*, 4, 653 (1908).

machine as shown in Fig. 255.¹⁵ The die itself is made the cathode. On the application of about 200 volts direct current across the electrode terminals, water passes to the die surfaces and prevents the clay from sticking. It has been found that further beneficial results may be had by modulating the direct current applied with a pulsating current of fairly high frequency, the amplitude of the modulating current being so regulated that a reversal of polarity never occurs. Best results are obtained by adding a small amount of electrolyte to the clay during its preparation.

Electrical lubrication has been applied for the purpose of reducing the draft in plowing. The plowshare is charged negatively and the ground positively. Under favorable conditions the plowshare is lubricated continuously by a thin film of water. The current can be obtained from a generator carried on and driven by the tractor drawing the plow. Crowther and Haines¹⁶ found that under laboratory conditions the friction with the most favorable circumstances was reduced more than 30 per cent, but concluded that for field use the costs do not justify the adoption of the method. They used a 110-volt generator and consumed 2 to 4 amp.

Electric Tanning. Electric tanning of leather¹⁷ by bark extracts has appealed to tanners because it is much more rapid than the conventional diffusion process, but it has found little commercial application, largely because of the anodic oxidation of the tannin. The electrical process was used in 1874 in Leningrad (then St. Petersburg) by de Meritens, who used 600 tan pits with a layer of carbon at the bottom for anode, placing on top of this alternate layers of hides and tan bark, with a sheet of tin on the top of the stack as cathode. Schwerin attempted to overcome anodic oxidation of the tannin by surrounding the electrodes with diaphragms.

Anodic Deposition of Rubber. The term "anode process" designates a fundamental method for producing directly from rubber latex articles and coatings of unmasticated rubber. Rubber latex is a milky exudation, from the bark of rubber trees, composed of tiny particles of rubber suspended in a water phase or serum. As it comes from the trees the latex is unstable and coagulates easily, but when stabilized with 2 to 3 per cent ammonia, by weight of dry rubber content, it can be shipped and stored for long periods of time.

¹⁵ J. O. Everhart, *J. Am. Ceram. Soc.*, 17, 272 (1934).

¹⁶ E. M. Crowther and W. B. Haines, *J. Agr. Sci.*, 14, 221 (1924).

¹⁷ S. Rideal and A. P. Trotter, *J. Soc. Chem. Ind.*, 10, 425 (1891); J. Buse, *ibid.*, 19, 57 (1900); E. K. Rideal and U. R. Evans, *ibid.*, 32, 633 (1913); O. J. Williams, *J. Am. Leather Chem. Assoc.*, 8, 398 (1918).

The rubber particles in the latex are charged negatively and under the influence of an electric current will migrate toward the anode, as was first shown by Victor Henri, in 1907. In 1909 Cockerill proposed to coagulate rubber electrically; this did not prove successful commercially, but a little later Clignett did substitute electrical for acid coagulation at the plantation. These processes, however, served the purpose of condensing and stabilizing the latex for transporation and storage. With the discovery of a method for stabilizing the fluid latex with ammonia, interest was renewed in electrical deposition, but essentially for the purpose of forming rubber articles and for coating articles with rubber.

The fundamentals of anodic deposition of rubber have been discussed by Sheppard and Eberlin.¹⁸ The cataphoretic migration of the rubber and associated "filler" particles is only a part of the change taking place in the cell. There are also electrolytic ions that discharge or tend to discharge at the anode. In the ammoniated latex, hydroxyl ions tend to discharge at the anode with the resultant liberation of oxygen. The nascent oxygen produces harmful changes in the rubber and causes porous structures. This difficulty can be overcome in various ways. One method consists in supplying some material like pyrogallol that oxidizes more easily than the rubber. Another method is to have other anions present, which have a lower discharge potential than the hydroxyl ions, and whose discharge generates innocuous or useful products. Sulphydrate, SH^{--} , and polysulphide ions, S_x^{--} , are very useful in this connection, for their discharge yields sulphur, which is a valuable ingredient in the subsequent vulcanization. Another method for avoiding oxygen evolution is to use anodes of metal which corrode and form stable oxides compatible with the rubber deposit. Zinc is the most satisfactory of such metals, but magnesium and cadmium can also be used. Copper anodes likewise prevent oxygen evolution, but the cuprous ions which are formed lead to a very rapid breakdown of the rubber. Another method consists in depositing the rubber on a porous diaphragm surrounding the anode, but in such a way that the oxygen evolved at the anode does not reach the rubber deposit.

Anodic deposition of rubber alone would afford only a very limited application of the process, for rubber requires sulphur for vulcanization, and the elastic and mechanical properties can be modified and controlled by the incorporation of various "inert" fillers, in the form of finely divided solids. It is a fortunate fact that sulphur, pigments, fillers, and softeners in finely divided form can be mixed with rubber

¹⁸ S. E. Sheppard and L. W. Eberlin, *Ind. Eng. Chem.*, **17**, 711 (1925); S. E. Sheppard, *Trans. Am. Electrochem. Soc.*, **53**, 47 (1927); *India Rubber World*, **73**, 193 (1926).

latex to form staple dispersions and that the mixed "compound" can be deposited substantially in the proportions in the mix. This is due to the fact that in cataphoretic migration the velocities of particles of different size do not differ greatly, and further that the velocities of different materials are not greatly different.

The process for commercial deposition has been described by Beal.¹⁰ A latex mix adjusted for anode deposition may, for example, contain 35 per cent by weight of rubber and compounding ingredients, about 20 g. per liter of ammonia, and 30 g. per liter of ammonium, potassium, and sodium salts, the larger part of which is ammonium chloride. The latex mixture is placed in the anode compartment of a diaphragm cell,

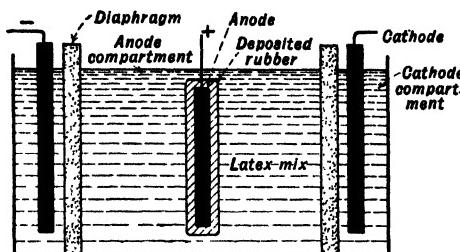


FIG. 256. Cell for anodic deposition of rubber.

Fig. 256. The cathode compartments are filled with slightly alkaline water. An anode of zinc or galvanized iron is immersed in the latex, and cathodes are placed in the cathode compartments. When a unidirectional e.m.f. is applied across the electrodes the suspended rubber and compounding ingredients move to the anode, where they are deposited. During continued deposition the e.m.f. impressed across the wet coagulated deposit on the anode removes water from it by electroendosmotic action, and compacts the deposit until it contains about 40 per cent water. This water content is sufficient to maintain the electrolytic conductance of the deposit and thus permit the deposition to continue.

The deposition factor of latex mixes increases rapidly with concentration. For example, 35 per cent mixes of normal pH and conductance may have deposition factors of 1.2 to 1.5 g. of dry deposit per amp-min., but, when the concentration is increased to 55 per cent, the deposition factor is often 2 to 4 times as great. A rate of 1.5 g. per amp-min. is over 2,400 g. per faraday, which is about 73 times the theoretical cathodic deposition rate of zinc.

Anode electrodeposition of rubber is particularly well suited for the application of soft and hard rubber coatings to odd-shaped metal arti-

¹⁰ C. L. Beal, *Ind. Eng. Chem.*, **25**, 609 (1933).

cles. The process is also applicable to the production of rubber articles up to $\frac{1}{4}$ in. in wall thickness. The rubber is deposited on forms of zinc or of other metals coated with zinc. Many relatively thin rubber articles, such as balloons, gloves, and fountain-pen sacs, that have long been made by the repeated dipping of forms in cement, some requiring hours to build up, can be made by anodic deposition in a few seconds or minutes. The process is also excellently suited for lining or coating metal parts with rubber for corrosion resistance. If a permeable membrane is placed around the anode the rubber particles will be deposited on it instead.

Anode rubber has high strength and durability. Tensile and elongation data such as 5,900 lb. per sq. in. at 970 per cent elongation are characteristic of anode rubber but difficult to obtain with masticated rubber.

CHAPTER XXII

MISCELLANEOUS ELECTROCHEMICAL PROCESSES

ANODIZING OF METALS

Anodic Oxidation of Aluminum. In the past few years the anodic oxidation of aluminum and its subsequent dyeing have reached considerable importance. It is not an electroplating process, but the oxidation is conducted in a manner very similar to that of electroplating except that the aluminum is made the anode in the cell instead of the cathode. Like electroplating it also supplies a finishing coat to the metal.

When aluminum is exposed to the atmosphere it soon protects itself against further oxidation by the formation of a thin oxide film. Such a film can also be prepared by chemical means, especially by electrochemical means by anodic oxidation. Such electrochemically prepared films have long been used in aluminum rectifiers. Lately the electrochemical condenser has come into wide use; it consists of an aluminum anode, an oxide film on its surface acting as a dielectric, and an electrolyte forming the second plate of the condenser. The current conductor to the electrolyte may also be made of aluminum.

The useful films in electrolytic rectifiers and condensers are very thin because they block the passage of the oxide-forming current. The films are usually made in solutions of boric acid or ammonium borate. If a different type of electrolyte is employed the film may have a sufficiently low resistance in the electrolyte to permit the building up of a relatively thick oxide coating, perhaps 0.001 in. in thickness or even more. Such films when properly prepared offer protection not only against corrosion but also against abrasion; in addition, they may have pronounced absorptive properties, so that they may be dyed almost any color.

A variety of electrolytes have been proposed for this purpose;¹ those in present use have been tabulated by Edwards² and are given in Table XXXV.

¹ A. Jenny, trans. by W. Lewis, *Anodic Oxidation of Aluminum and Its Alloys*, Chemical Publishing Company, New York, 1940.

² J. D. Edwards, *Trans. Electrochem. Soc.*, 81, 341 (1942).

TABLE XXXV

TYPICAL PROCEDURES FOR ANODIC OXIDATION OF ALUMINUM

Electrolyte	Typical Operating Characteristics	Comments
Chromic acid, 3%	40 to 50 volts, 3 amp./sq. ft.	Coating gray in tint and usually about 0.001 in. (0.0025 mm.) thick.
Oxalic acid, 3%	65 volts, 12 amp./sq. ft.	Coating cream colored; thickness up to about 0.001 in. (0.025 mm.).
Sulphuric acid, 15%	15 volts, 12 amp./sq. ft.	Coating white or transparent; thickness up to about 0.001 in. (0.025 mm.).
Boric acid plus ammonium borate	50 to 500 volts	Coating usually thin and iridescent; thickness proportional to formation voltage.

In the United States the sulphuric acid process has met with favor. The article is first freed from oil and grease by washing in an organic solvent such as gasoline or benzene, or by treatment in an alkaline cleaning solution, as, for instance, a 15 per cent sodium hydroxide solution. After cleaning, the aluminum article is washed in water, or, if it is an aluminum alloy containing copper, it is washed in dilute nitric acid.

The article is then placed in the electrolytic tank as anode. The electrolyte concentration ranges from 7 to 60 per cent sulphuric acid; the temperature is usually kept between 15 and 30° C. (60 and 86° F.). It is necessary to provide means for cooling the bath in order to keep the temperature sufficiently low. The time of treatment is from 10 to 15 minutes.

Upon removal from the oxidizing bath the articles are washed in water and then dipped into dilute ammonia to neutralize any remaining acid, and again rinsed in water.

The oxide films are highly absorptive and permit coloring by dyes for decorative purposes. The color penetrates the oxide coating throughout its depth and is not easily dissolved except by solutions that attack the coating itself.

Where the coating is to serve chiefly for protection, the porosity may not be desirable; then the pores of the oxide coating can be sealed by treatment with hot or boiling water. The color and appearance of the coating are not materially changed, but the coating can no longer be stained. Hot solutions containing nickel or cobalt acetate may also be used for sealing the pores, or a pigment like lead chromate may be precipitated in the pores.

Coatings on Other Metals. Considerable study has been devoted to coatings on magnesium, but no oxide coating methods have been devel-

oped for magnesium which are as effective as those for aluminum. This is due in part at least to the difference in the chemical behavior and physical properties of the two oxides. One of the best anodic treatments is that prepared by Buzzard and Wilson.³ The electrolyte is an acid mixture with a pH of 4.0 to 4.8 containing about 10 per cent sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, and from 2 to 5 per cent monosodium phosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. After cleaning or pickling the magnesium surface is made anode at a current density of 5 to 10 amp. per sq. ft. at a temperature of 50° C. (122° F.) for a period of 30 to 60 min.

Studies have been made of coatings on other metals, including zinc and iron, but these are of lesser importance as regards the present state of development. These coatings are reviewed by Edwards.⁴

ELECTROLYTIC POLISHING AND ETCHING

In preparing metallurgical specimens by grinding, polishing, and etching, for microscopic examination, the polishing phase can in a number of cases be accomplished successfully electrolytically,⁵ and it is to be expected that considerable development will follow. The usual mechanical method is time-consuming but in the hands of an expert produces excellent results. Electrolytic polishing will often produce equally satisfactory results in less time and the personal factor is of less importance; ferritic and austenitic stainless-steel alloys can be polished electrolytically with a degree of perfection difficult to attain by mechanical means.

In electrolytic polishing or etching, the surface to be treated is made the anode in a suitable electrolyte. The cathode is commonly carbon or stainless steel, but a variety of materials should be suitable. The polishing of metals is apparently accomplished by anodic solution of high points of the surface of the metal. The corrosion products probably form a poorly conducting film which adheres to the depressions but exposes the projections. Finally the metal surface is leveled to a microscopic plane, which may have a degree of polish equal to or better than that obtained on a metallographic polishing wheel.

A number of electrolytes used in the polishing of low-carbon steels have been studied by Imboden and Sibley.⁶ One of several satisfactory baths reported contained 40 per cent sulphuric acid, 46 per cent phos-

³ R. W. Buzzard and J. H. Wilson, *Natl. Bur. Standards J. Research*, **18**, 83 (1937).

⁴ J. D. Edwards, *loc. cit.*

⁵ G. E. Pellissier, H. Markus, and R. F. Mehl, *Metal Progress*, **37**, 55 (1940); G. F. Meyer, G. D. Rahrer, and J. R. Vilella, *Metals & Alloys*, **13**, 424 (1942); O. E. Brown and C. N. Jimison, *Metal Progress*, **40**, 298 (1941).

⁶ R. L. Imboden and R. S. Sibley, *Trans. Electrochem. Soc.*, **82**, 227 (1943).

phoric acid, 4 per cent dextrose, and 10 per cent water. Current densities range from 1.5 to 4.5 amp. per sq. in. (23 to 70 amp. per sq. dm.) at temperatures of 28 to 40° C. (82 to 104° F.).

A solution containing perchloric acid, acetic anhydride, and water has been reported by Merchant.⁷ Mixtures of perchloric acid with any organic material are potential explosives, and special precautions are necessary in the preparation and use of the solution. Uhlig⁸ obtained maximum polishing with an electrolyte consisting approximately of 42 per cent of phosphoric acid, 47 per cent glycerine, and 11 per cent water by weight. The surface to be polished is made anode with a current density of at least 0.1 amp. per sq. in. (1.5 amp. per sq. dm.). The solution is used at 100° C. (212° F.) or higher.

A method for etching brass for metallographic examination has been developed by Williams and Rieger.⁹ They obtained best results with a solution containing 10 parts 0.10 M ammonium acetate, 30 parts 14 M ammonium hydroxide, 30 parts 0.50 M sodium thiosulphate, and 30 parts distilled water. The solution does not attack the sample unless it is made anodic, but at a current density of about 2 amp. per sq. in. (31 amp. per sq. dm.) the etch is produced rapidly.

ELECTROLYTIC RECTIFIERS

It has long been known that certain metals when used as electrode in a suitable electrolyte offer a very high resistance to the flow of current from the electrode to the electrolyte but practically no resistance to the flow of the current in the opposite direction. Such a metal acts as a check valve for either alternating or direct current, unless a very high voltage is used.

A considerable number of metals exhibit this valve effect, and probably all metals possess the property to some degree when placed in a suitable electrolyte. The metals that show it more pronouncedly than most others are aluminum, tantalum, tungsten, bismuth, and magnesium, but only aluminum and tantalum have found successful commercial application.

Aluminum used as anode in electrolytes such as very dilute ammonium borates, carbonates, phosphates, and the corresponding salts of the alkali metals may form films which have a breakdown resistance of 600 volts. The anodes become coated with a film of oxide, or hydrated oxide, but the exact nature of the film does not seem to have been estab-

⁷ M. E. Merchant, *Metal Progress*, **37**, 559 (1940); *Metals & Alloys*, **13**, 430 (1942).

⁸ H. H. Uhlig, *Trans. Electrochem. Soc.*, **78**, 265 (1941).

⁹ G. C. Williams and G. Rieger, *Trans. Electrochem. Soc.*, **77**, 26 (1940).

lished. At moderate voltages the anions cannot penetrate this film to discharge their electrons, and consequently no current flows; but at very high potentials, anions give up their charge even though they cannot reach the metal, the electrons passing through the film layers. During this discharge a pale light is formed around the anode, caused by myriads of small sparks. Finally the film is disrupted with resultant sparking and the production of crackling noises.

If after the metal has been used as anode it is used as a cathode it may react in several ways. In some cases the insulating layer is readily destroyed, but in others, particularly if the oxide film is not readily reduced, as in aluminum and tantalum, the film persists but it allows H^+ ions to discharge.

Several theories have been proposed to account for this phenomenon in which anions cannot discharge through the film but H^+ ions can. The theory most commonly referred to is that of Schulze,¹⁰ who believes that the film on an aluminum electrode consists of a porous layer of oxide or hydroxide, partially filled with gas, which is impermeable to all except H^+ ions. When the aluminum is cathode, according to this theory, the H^+ ions are able to penetrate the film and become discharged at the surface of the metal. The film, therefore, permits the flow of electrons from, but not to, the electrode.

MacGregor¹¹ is of the opinion that the mechanism of rectification can be explained by the formation of "cushions" of gas between the surface of the anode metal and a thin overlying oxide-hydroxide film. The electrons are considered to penetrate the gas, pierce the oxide film, and pass as cations through the solution. Lilienfeld and his associates¹² conclude that the behavior of the anodic layer corresponds to that of a dielectric containing a large number of polar compounds, and that the properties of the layer are determined by the potential applied, the current being a secondary factor.

Rectifiers. The subject of electrolytic rectifiers has been studied by Holler and Schrot.¹³ The electrolytes which have been found satisfactory for aluminum rectifiers are, in general, the alkali borates, tartrates, phosphates, oxalates, citrates, and carbonates, but unfortunately most of them have a low conductivity, and the addition of small amounts of the strong acids or salts of the heavy metals accelerates deterioration of the aluminum electrode. The electrodes used opposite the aluminum

¹⁰ G. Schulze, *Z. Elektrochem.*, **14**, 333 (1908); *Trans. Faraday Soc.*, **9**, 266 (1913).

¹¹ M. E. MacGregor, *Nature*, **125**, 128 (1930).

¹² J. E. Lilienfeld, L. W. Appleton, and W. M. Smith, *Trans. Am. Electrochem. Soc.*, **58**, 225 (1930).

¹³ H. D. Holler and J. P. Schrot, *Bur. Standards Tech. Paper* 265, 1924.

have generally been lead, iron, or carbon. The cell container may be made of glass, lead, or iron, and if one of the last two, the container may also serve as electrode.

A commercial aluminum rectifier has been described by Holland.¹⁴ An iron-silicon alloy of the nature of Duriron, containing about 14 per cent of silicon, was found most satisfactory for one electrode. It was also found that if the aluminum electrode contained not less than 0.05 per cent of copper, but not more than 0.15 per cent, the rectifier has maximum current delivery and maximum life. Dibasic ammonium phosphate is used as the electrolyte, but its conductance is greatly improved and

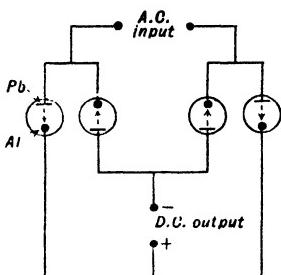


FIG. 257. Four rectifiers connected for full-wave rectification.

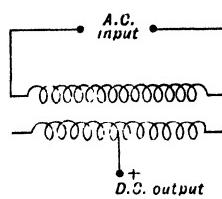


FIG. 258. Schematic diagram for full-wave rectification with a three-electrode rectifier.

the heating of the electrolyte is reduced by the addition of a phosphate or other salt of potassium; and by the addition of a suitable amount of either malic or citric acid, the capacity for holding aluminum in solution is increased very much and the useful life of the rectifier is greatly extended.

If the current density on the aluminum electrode is sufficiently high the film forms in a few seconds after the current is turned on.

Tantalum is also used as an electrode in commercial rectifiers. The opposite electrode is generally lead or lead peroxide. Potassium carbonate gives fairly good results, but sulphuric acid, of approximately the same concentration as in storage batteries, is used in commercial rectifiers. The rectifying property of tantalum is acquired almost immediately after the application of an alternating current to a fresh strip of the metal. A transformer is combined with the rectifier to reduce the line voltage to the proper operating amount.

Single rectifiers give but half-wave rectification, whether of the aluminum or tantalum type; but by connecting four rectifiers as shown in Fig. 257 full-wave rectification is obtained. A rectifier with two

¹⁴ W. E. Holland, *Trans. Am. Electrochem. Soc.*, **53**, 195 (1928).

aluminum or tantalum electrodes and one lead electrode will give full-wave rectification when constructed and connected as shown in Fig. 258.

Anode films on aluminum are also used in electrolytic condensers. The condenser consists of an aluminum anode; the oxide film serves as the dielectric; and the electrolyte serves as the second plate of the condenser. A current conductor to the electrolyte completes the condenser.

ELECTROLYTIC WATER TREATMENT

Electrolytic Water Sterilization. Water can be sterilized in a suitably constructed electrolysis cell in which bacteria are killed by the nascent oxygen liberated at the anode. A commercial cell has been developed by the United States Ozone Company of America. The electrode box, Fig. 259, consists of a series of metallic plates made of an iron-aluminum alloy which serve as electrodes. The plates are separated by marginal gaskets of varying thickness determined by the nature of the water treated. The alternate ends of the plates are slotted so that the water as it goes through the box passes over the entire treating area.

A cell for operation on 110 volts direct current consists of 21 plates making a potential of 5.5 volts between adjacent plates. The cell is provided with flushing cocks, which, when opened once each day, permit a flushing out of any sediment formed. A double-pole double-throw switch is provided for the purpose of reversing the polarity of the plate surfaces daily. When this is attended to, the necessary work of cleaning the plates periodically is greatly reduced. The energy consumption averages in the neighborhood of 200 watt-hr. per 1,000 gal.

A complete sterilizing unit includes in addition to the electrolysis cell a coagulation or sedimentation tank and a set of filters for removing suspended particles from the water after it has passed through the electrolysis cell.

The operation of the unit is automatic. A low-pressure contact valve consisting of a hydraulic piston is operated in synchronism with the flow of water. The piston operates an automatic switch which controls the electrical connections. In this manner the current is cut on and off with opening and closing of the main water valve or faucet.

Electrolytic sewage treatment has not found much adoption. One of the most promising methods is the Landreth direct oxidation process,

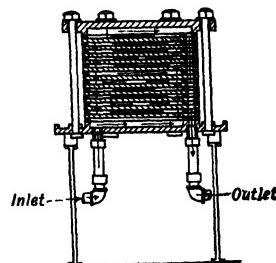


FIG. 259. Electrolysis cell for water sterilization.

described by Creighton and Franklin.¹⁶ Butterfield¹⁶ arrived at the conclusion that the expenses involved in electrolytic sewage treatment do not justify the results obtained.

The Katadyn process for the sterilization of water was developed in Germany by G. A. Krause.¹⁷ The method is based on oligodynamy, the property of minute traces of certain metals, particularly silver, to sterilize water. In one method the silver is introduced into the water by anodic solution in a cell called the activator, shown in Fig. 260. It consists of an iron tank lined with a special insulating material in which are placed a number of silver electrodes. In order to avoid polarization,

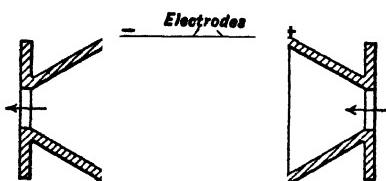


FIG. 260. Water sterilizer equipped with silver electrodes.

the current is reversed at definite intervals. The voltage is not allowed to exceed 1.6 volts so as to avoid electrolysis of water. The current varies from 0.02 to 10 amp., according to the size of the plant. The energy consumption is so small that its cost may be disregarded for all practical purposes; under the most

unfavorable conditions it is less than 0.001 kw-hr. per ton of water treated. The cost of silver consumed ranges from 0.1 cent per ton of water for drinking purposes to 1.5 cent per ton for highly bactericidal rinsing water to be used in food and beverage plants. The action of the silver is not immediate but requires from 30 minutes to several hours, depending upon the quality of the water and the bacteria involved. The small amount of silver introduced into the water is said to have no harmful effect on the human system.

The process is employed in Germany for sterilization of water used for drinking purposes, in swimming pools, and ice plants, and for the preparation of highly bactericidal water for washing, rinsing, and disinfecting equipment in beverage and food plants, in the vinegar industry, and in the manufacture of pharmaceuticals. A unit is installed in the swimming pool of the Congressional Country Club at Washington.

Electrolytic Purification of Water. The amount of dissolved substances in water varies from about 0.2 to 1.0 per cent. Purification by distillation involves the removal of the large amount of water from the small amount of impurity. The principle of removing the small amount of dissolved substance from the water has appealed to many investigators. If the impurities are electrolytes, as is usual, then it is possible

¹⁶ H. J. Creighton and B. Franklin, *J. Franklin Inst.*, **188**, 157 (1919).

¹⁶ E. E. Butterfield, *Proc. Am. Soc. Munic. Improvements*, **35**, 253 (1930).

¹⁷ Anon., *Chem. & Met. Eng.*, **41**, 372 (1934).

to remove the dissolved substances by electrical methods. The classical experiments of Hittorff on transference numbers demonstrated that the concentration of electrolytes, separated by a diaphragm, is altered upon the passage of an electric current.

Cells for the purification of water by electrical means have been described by Behrman¹⁸ and by Billiter.¹⁹ The cells consist of three compartments separated by two diaphragms. The cells may be rectangular in plan with two parallel diaphragms, or they may be circular with two concentric diaphragms. The two outer compartments contain the electrodes. In the three-compartment cells the water passes from the middle compartment of the first cell to the middle compartment of the next cell, and so on through a cascade of cells, which may amount to ten cells.

Under the influence of the direct current the positive ions pass through the diaphragm into the negative compartment and the negative ions into the positive compartment. The first four cells are connected in series across a 220-volt d-c. line; similarly, the next three cells in series, then the next two cells, and finally the last cell across 220 volts.

The efficiency of the cells decreases as the salt content of the water increases. If the original water contains 250 to 300 mg. per liter of dry residue on evaporation, the output of the 10 cells in series is about 5 gal. per hr. per sq. ft. of cell cross-section. Rectangular cells are of the filter-press type.

The Billiter cell is cylindrical with diaphragm areas as great as 10 to 15 sq. ft. The cells may be operated on voltages ranging from 7 to 220. These direct electrolysis cells will purify waters containing from 150 to 600 mg. per liter of salts, the purified water containing 6 to 9 mg. per liter with an electrical conductance as low as $2 \text{ to } 10 \times 10^{-7}$ mho-cm., at a pH of 6.8 to 7.2. For waters with more than 600 mg. per liter salts, four to six cells are operated in series at 220 volts. With special precautions it is possible to obtain a water with a conductance of $1.2 \text{ to } 1.8 \times 10^{-7}$ mho-cm., which is lower than that of doubly distilled water.

Current and energy efficiencies are low, the current efficiencies usually being under 20 per cent. The current efficiency is independent of the temperature. The low efficiency is due chiefly to the fact that the ions that have migrated to the electrodes diffuse back into the central compartment. The diffusion can be counteracted by keeping the water in the central compartment at a slight hydrostatic head so that the flow of the water through the diaphragms opposes that of the ions dis-

¹⁸ A. S. Behrman, *Ind. Eng. Chem.*, **19**, 1229 (1927).

¹⁹ J. Billiter, *Trans. Electrochem. Soc.*, **60**, 217 (1931); **70**, 409 (1937).

charged at the electrodes. By applying the above scheme about 10 to 40 per cent of the raw or partially purified water is carried away with the salts removed. Results of tests on cells have been published by Bartow and Jebens.²⁰

In the filter-press type of cells, diaphragms have consisted of cloth, plain or impregnated, asbestos cloth, chrome leather, and ceramic plates. Anodes are made of graphite, carbon, or magnetite.

ELECTROCULTURE

A number of investigators have been interested in the question whether plant growth can in some way be influenced by the action of electricity. The results of the more scientific attempts have been summarized by Cooper²¹ and by Matthews.²² Lemström was puzzled, as others had been, by the luxuriance of plant growth in the polar regions. The difference between the growth in these regions and that in more temperate climates did not seem sufficiently explained by the longer duration of daylight in summer, and Lemström turned to the electrical conditions in the atmosphere as a possible explanation. Electrical conditions near the polar regions were considered to be somewhat abnormal as shown by the aurora borealis, and it was considered that there might be some intimate connection between the luxuriance of plant growth and the electric currents flowing from the atmosphere to the earth. Lemström started the first scientific investigation of this subject and published his results,²³ but a number of other investigators including Sir Oliver Lodge had also become interested in the subject.²⁴

It is extremely difficult to make exact investigations, for it is almost impossible to obtain two control plots identical in all respects except that one is subject to electrical effects and the other is not, and this difficulty has been chiefly responsible for the dearth of scientific data on the subject.

Usually the atmosphere is charged positively with respect to the earth and the potential increases with heights above the ground. Above

²⁰ E. Bartow and R. H. Jebens, *Ind. Eng. Chem.*, **22**, 1020 (1930); E. Bartow, *J. Am. Waterworks Assoc.*, **22**, 1115 (1930).

²¹ W. R. Cooper, *Electro-Chemistry Related to Engineering*, p. 113, D. Van Nostrand and Company, New York, 1923.

²² R. B. Matthews, *Electro-Farming*, Ernest Benn, London, 1928. This book gives numerous references to the literature.

²³ S. Lemström, *Electricity in Agriculture and Horticulture*, "The Electrician" Printing and Publishing Co., London, 1904.

²⁴ L. B. Atkinson, *J. Inst. Elec. Eng.*, **59**, 13 (1920); H. G. Dorsey, *Elec. World*, **62**, 1217 (1913).

open level ground the potential gradient is about 70 volts per foot. The reason for this electrification has not been adequately explained, but positive and negative ions are present, the positive ions moving downward and the negative ions upward under the normal conditions of the earth being negative. There is thus a continuous current, from the atmosphere to the earth, which has a value of approximately 2.5×10^{-16} amp. per sq. cm. or 1×10^{-8} amp. per acre.

Lemström placed a highly charged network of wires above the ground, and, for the sake of obtaining a fairly uniform electrical field, the distance between the wires was made equal to one-half their height above the ground. It is usual to make the network positive, but negative electrification has also been found to be effective, from which fact it would appear that alternating current would be satisfactory, but most of the investigational work has been carried on with unidirectional current. The e.m.f. used was 50,000 volts or more. At one time a firm in England, the Agricultural Electrical Discharge Company, supplied complete equipment for electrifying a field for farmwork; they placed the wires 18 ft. above the ground and 24 yd. apart. The electrical discharge is usually applied for a certain number of hours per day in dry weather.

Results have been published, giving increase in yields from 10 to above 50 per cent; but, as pointed out by Cooper, such figures require a most careful confirmation. In a report of the Electro-Culture Committee of the Board of Agriculture, England, results are given for a period covering a number of years, and these show large variations. In one case the increase in oats was reported to be 57 per cent, and that of barley 35 per cent. On the other hand, the increase in some instances has been very small and even negative. For potted plants it appears that if the current exceeds a certain value per plant it is definitely harmful.

From the practical point of view it is necessary that the increase in yield should show a profit after meeting all costs of working, including interest and depreciation on the capital cost of the plant. It is estimated that a 20 per cent increase in crops would leave practically no margin of profit.

It can safely be said that the project is still in its infancy and that at present it is questionable whether any real gains are obtained.

DEUTERIUM AND DEUTERIUM OXIDE

Deuterium, also called heavy hydrogen, was discovered by Urey²⁵ and his associates at Columbia University. The atomic weight of

²⁵ H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.*, **39**, 164, 864 (1932); **40**, 1 (1932).

deuterium is twice that of ordinary hydrogen (protium). This difference gives deuterium and its compounds, such as deuterium oxide (heavy water), slightly different properties from those of protium and its compounds. The discovery of deuterium is so recent that its full implications are not understood. The density of heavy water is $1.1056^{\frac{20}{4}}\text{C}.$

The first deuterium was isolated by fractional distillation of liquid hydrogen. The boiling point of deuterium is 23.5°K . (-249.6°C .), whereas that of hydrogen is 20.4°K . This method of separation was very expensive, but an electrolytic method for concentration of deuterium oxide was developed by Washburn and Urey.²⁶

When water is decomposed into its elements by electrolysis, heavy water remains in more concentrated form in the cell, while the greater portion of the lighter hydrogen passes off as a gas. If water is continuously added to the cell to keep the level constant, a steady state is attained and no further increase in the concentration of heavy water in the cell occurs. It is economical for the electrolytic production of heavy water from ordinary water to add fresh water to the cell to keep the volume constant until two or three times the volume of the cell has been electrolyzed before reducing the volume of the water without further addition.

The water in the electrolysis cell is made conductive by the addition of sodium hydroxide or potassium hydroxide. A 5 molal (about 18 per cent) solution is a suitable concentration. When the final concentration of heavy water is obtained the hydroxide is neutralized with carbon dioxide (to liberate as water the heavy hydrogen held chemically combined in the hydroxide) and then distilled. If it is desired to separate the heavy hydrogen, the solution is electrolyzed and the heavy hydrogen is collected.

As electrolysis proceeds in the cells, the hydrogen given off carries an appreciable amount of deuterium, so that for efficient operation this is burned and the water thus obtained is electrolyzed in other cells.

The cells used are simple containers of metal or glass, with two electrodes passing through the top. The electrodes are rods or strips of iron or steel and are usually nickel plated to avoid corrosion, but it is reported that unplated steel electrodes function more efficiently. Washburn²⁷ and his associates used an electrolyzer of the filter-press type, having 56 nickel-plated cast-iron plates, separated by asbestos cloth diaphragms. The electrolyte was an 18 per cent solution of sodium hydroxide. The electrolyzer operated at 12 to 15 amp. at 115 volts, at

²⁶ E. W. Washburn and H. C. Urey, *Proc. Natl. Acad. Sci. U. S.*, **18**, 496 (1932).

²⁷ E. W. Washburn, E. R. Smith, and F. A. Smith, *J. Research, Bur. Standards Research Paper 729*, 1934.

about 60 deg. C. (140 deg. F.). The liberated gas passed through metal pipes surrounded by ice water to reflux as much as possible of the heavier water carried as vapor and liquid by the stream of gas.

It is advantageous to start electrolysis by using electrolyte from commercial hydrogen-oxygen cells in which an equilibrium state has been reached. A steady state is attained in such cells after an amount of water equal to approximately 10 times the volume of the cell has been electrolyzed, after which no isotopic fractionation occurs.

Ordinary water contains about 175 deuterium atoms in one million hydrogen atoms. The electrolyte from commercial hydrogen-oxygen cells contains about 500 deuterium atoms per million hydrogen atoms. The name deuterium has been widely accepted to designate heavy hydrogen, but for symbols, both D and H² are used.

The discovery of two hydrogens, one with a density double that of the other, may have far-reaching significance. There are about 350,000 known chemical compounds, and of these about 90 per cent contain hydrogen. The discovery has opened a vast field for investigation.

A triple-weight hydrogen, H³, has also been identified. Work completed thus far indicates that, in ordinary hydrogen, about one atom in 10 billion is triple-weight.

INJURIES FROM ELECTRIC SHOCK

About 2,500 persons suffer from electric shock annually, and about 50 per cent of the cases prove fatal. As a consequence there has been a stimulus for careful study as to the dangers involved and the causes of death, much of the investigation having been done at the Johns Hopkins University, Baltimore, Maryland.²⁸ Case analyses have shown that individuals between 15 and 30 years of age are most likely to be the victims, and that more men are injured than women.

Experiments on anesthetized rats indicate clearly that at low voltages, up to 500 volts, a-c. shocks are more deadly than d-c. shocks; but on a 1,000-volt circuit, d-c. shocks at the corresponding voltage are more deadly. In either case the injury increases with increase in time and voltage.

The d-c. shocks on rats generally produced symptoms of irritation to the nervous system such as convulsions, whereas a-c. shocks showed paralysis of the posterior portion of the body directly after the shock. Such paralyzed animals never lived longer than two or three days;

²⁸ W. B. Kouwenhoven and O. R. Langworthy, *Elec. Eng.*, 50, 506, 929 (1931), 51, 242, 698 (1932); *J. Franklin Inst.*, 215, 1 (1933). Some of these articles give further references.

after death they showed an abnormally soft spinal cord, and microscopic examination of the cords revealed that an area of hemorrhage had severed nervous pathways.

Hemorrhages have also been found in the brains of men who have died as the result of similar shocks. Such hemorrhages are believed to be caused by the sharp rise in blood pressure which follows the breaking of the contact with an electric circuit. During the period of current flow, the blood collects in the veins, being squeezed from the heart and arteries by the contraction of the muscles in their walls. When the heart resumes its beating all this blood is suddenly forced back into the heart and arteries, often overtaxing the capacity of the arteries, resulting in the rupture of their walls.

In human beings, electric currents of 8 to 10 ma. are quite painful; 90 to 100 ma.²⁹ are considered dangerous. When a body forms part of an electric circuit the current passing through the body is determined by the voltage of the line, the ohmic resistance of the body, which in human beings amounts to about 200 ohms, and the contact resistance, which in the calloused palm of a laborer may be 100,000 ohms per sq cm. The contact resistance of the body is an important factor when dealing with low-voltage currents as used in residences. When a person who is well grounded comes into contact with a low-voltage circuit the value of the current may be sufficient to cause death. The majority of such accidents occur in bathrooms, damp cellars, around water and gas piping, and other places where local conditions reduce the contact resistance of the body to a negligible value. Accidents have been found to be more common during the summer months as a result of reduced protection by clothing, and the presence of perspiration which decreases the skin resistance. When contact is made with a high-voltage circuit, the contraction of the muscles is so violent that the victim may be thrown clear, but it is difficult if not impossible for the victim to release his hold in case of low-voltage shock, because the muscular contraction is steady instead of violent.

The path of the current through the body is an important factor. Generally, a current passing from arm to arm, or arm to leg, is more dangerous than a current passing from one part of an arm to another part of the same arm. However, several accidents are on record in which unconsciousness followed a shock between two fingers of the same hand or two points on the same leg.

Not only is the total current through the body an important factor, but the current density must also be taken into consideration. Laboratory experiments have shown that a small animal could not recover from

²⁹ One thousand milliamperes (ma.) = 1 amp.

a given shock as readily as a much larger animal. This may account for the belief that thin people are more susceptible to electric shocks than large individuals.

The heart and the respiratory center in the brain are particularly susceptible to injury by electric currents. The above-mentioned investigators conclude that death as an ultimate result of electric shock may occur from several different direct causes:

1. By asphyxiation caused by the prolonged muscular contraction.
2. By ventricular fibrillation ³⁰ of the heart, usually believed to be induced by low-voltage shocks.
3. By destruction of the nerve cells in the respiratory center of the brain.
4. By excessive increase in body temperature as a result of the Joule effect of the shock current.
5. By severe burns or other resulting complications.

Kouwenhoven and Langworthy ³¹ make the following important statement:

Competent authorities stress the fact that in electrical accidents death often is *only apparent*. Artificial respiration should be begun *immediately* following an accident and continued until the patient recovers or until the cessation of life as an actuality is evident by the onset of *rigor mortis*. Accredited reports list many successful resuscitations following the application of the Schaefer prone pressure method of artificial respiration, in one case success following an 8 hr. effort.

³⁰ "By ventricular fibrillation is meant the failure of the ventricles of the heart to beat with a coordinated rhythm; under this condition all individual muscle fibers of the heart contract asynchronously and accordingly no blood is circulated by that organ."

³¹ *Op. cit.*, 51, 696 (1932).

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